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Research Program:

Research Summaries 1982-1983

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NASA

REPORT TO THE CONGRESS
AND THE
ENVIRONMENTAL PROTECTION AGENCY
ON THE
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION'S
UPPER ATMOSPHERIC RESEARCH PROGRAM

JANUARY 1984

Dr. Watson's office
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INTRODUCTION

In compliance with the Clean Air Act Amendments of 1977, P. L. 95-95, the National Aeronautics and Space Administration (NASA) has prepared a report on the state of the knowledge of the earth's upper atmosphere, particularly the stratosphere, and on the progress of the NASA Upper Atmosphere Research Program (UARP). The report is composed of two parts. The first part is an assessment entitled "Present State of Knowledge of the Upper Atmosphere: An Assessment Report." The second portion of the report is the present document, which presents summaries of the objectives, status, and accomplishments of the research tasks supported under the NASA UARP. Together these documents form the fourth of a series of biennial reports, the first of which was made in January 1978.

Under the mandate contained in the FY 1976 NASA Authorization Act, NASA has developed and is implementing a comprehensive program of research, technology, and monitoring of the earth's upper atmosphere, particularly the stratosphere. This program is focused on expanding our understanding of this important region of our atmospheric environment and on developing our ability to assess potential perturbations, particularly to the ozone layer. Within NASA the UARP is in the Earth Science and Applications Division in the Office of Space Science and Applications. The long-term objectives of the present program are to perform research to:

(1) understand the physics, chemistry and transport processes of the upper atmosphere, and

(2) accurately assess possible perturbations of the upper atmosphere caused by man's activities

The NASA program involves analysis of data obtained by large satellite missions such as Nimbus-4, SAGE, Nimbus-7, and Solar Mesospheric Explorer as well as a variety of research tasks proposed by scientists from the university, government, and industrial research communities. In addition, the UARP sponsors periodic assessments of the state of our knowledge of the upper atmosphere and of the effects of specific perturbations such as chlorofluoromethane (CFM) releases, aircraft effluents, and other potential pollutants. Of greatest urgency at present is an assessment of the combined effects of continued increases in the atmospheric concentrations of $CFCl_3$, CF_2Cl_2, CH_3CCl_3, CO_2, NO_x possibly, and other gases such as N_2O and CH_4. Another goal is to understand the role of stratospheric ozone in the radiative heating and thus the dynamics of the atmosphere, and thereby to assess the importance of chemical-radiative-dynamical feedbacks on the meteorology and climatology of the stratosphere and troposphere. In the non-satellite portion of the program, activities generally fall into four broad categories: (1) field measurements (*in situ* and remote sensing techniques using ground-based instruments, aircraft, balloon and rocket platforms), (2) laboratory studies (gas kinetics, photochemistry, spectroscopy and the development of calibration standards), and (3) theoretical studies (1D, 2D and 3D models) and (4) data analysis (especially analysis of large satellite data sets). These areas represent approximately 50%, 20%, 20%, and 10% respectively, of the research program of $22.5M in FY83. Current research funding supports specific investigations in areas such as the following:

a. Determination of the distribution of trace gases in the upper atmosphere, with emphasis on those which influence the ozone balance.

b. Observations of the global distribution of ozone, its vertical profile, and temporal variations.

c. Improvements in the theory of upper atmospheric photochemical processes; validation of theory by comparison with measurements.

d. Improvements in the understanding of atmospheric dynamics and transport processes by both theory and measurement.

e. Determination of the characteristics of motions responsible for the exchange of air between the troposphere and stratosphere.

f. Determination of the geographic distribution and strengths of sources and sinks for stratospheric compounds.

g. Measurements of the ultraviolet solar irradiance and its temporal variations.

h. Laboratory studies in spectroscopy and chemical kinetics relevant to the interpretation of atmospheric measurements and to theoretical simulations of the atmosphere.

i. Development of new technological ideas, techniques, and instruments for use in upper atmospheric research.

Since the January 1982 report, substantial advances in our knowledge of the upper atmosphere have been made in each of the four major research categories. Laboratory studies have strengthened our knowledge of the chemical kinetics of stratospheric components, and have provided improved data on the spectroscopy of atmospheric gases for applications to atmospheric measurements of trace species. Many of the trace gases in the hydrogen, nitrogen, and chlorine chemical families which participate in the chemistry of ozone have now been detected in the stratosphere, while investigation of their spatial and temporal variations is underway.

In order to judge our understanding of the important chemical and physical processes that occur in the stratosphere, the theoretically predicted trace gas distributions are compared to experimental field observations. To date, the accuracy of the reported field measurement data has been difficult to assess and the reported data on the concentrations of most species show large scatter that can either be due to atmospheric variability or instrumental differences. Consequently, the comparison of observational data with theory is currently limited in scope. In order to be able to constrain or test the theoretical models, the reason for the scatter in the data must be understood. Therefore, it has been essential to perform a series of instrument intercomparisons under field conditions.

A highlight of the research program was an international balloon-borne intercomparison of remote sensing instruments conducted in two phases: (1) 13 instruments on four gondolas in Fall 1982, and (2) 17 instruments on four gondolas in Spring/Summer 1983. Complementary ground and aircraft based measurements were also performed. Nearly simultaneous measurements were made on a wide variety of atmospheric species which are the key to understanding the chemistry of the stratosphere, including the hydroxyl radical, nitric acid, nitric oxide, nitrogen dioxide, hydrogen chloride, hydrogen fluoride, water vapor, methane and ozone. Data obtained during the campaigns are currently being analyzed.

The intercomparison will not only show how good the agreement is between the instruments, (principally grating and Fourier transform infrared spectrometers), but will also test the different methods of data reduction and analysis used by the various scientific groups involved. The intercomparison is intended to assess the accuracy and precision of measurements that can then be used to test our understanding of atmospheric photochemical phenomena. The data should provide the most stringent test to date of some facets of photochemical theory.

An international balloon-borne intercomparison of a variety of ozone measuring devices was conducted in July 1983. Half a dozen instruments, consisting of research in-situ and remote sensing devices and operational sondes participated in the inter-comparison. The results are being analyzed.

Similar water vapor intercomparisons were conducted in May 1981 and September 1983 to determine if the reported differences in vertical profiles were due to atmospheric variability or the lack of precision and accuracy of the measurements data. Four balloons, carrying photofragmentation, frost point hygrometer, mass spectrometer and cryogenic sampling in-situ instruments along with two infrared radiometers, participated in each of these intercomparisons. Much has been learned from the May 1981 campaign about the quality of data from these instruments. However, a few unresolved issues remain which will hopefully be resolved from the data of the September 83 campaign.

Other recent accomplishments of the field measurements program include direct observation of OH from a balloon by UV laser induced fluorescence and by far infrared emission spectroscopy, ground-based observations of stratospheric ClO and HO_2 using microwave radiometry, direct observations of the penetration of ultraviolet radiation in the stratosphere, and a demonstration of the reel-up/reel-down technique for repeating _in situ_ vertical soundings during a single balloon flight. Atmospheric dynamics studies are continuing on (1) the exchange of air between the troposphere and stratosphere using aircraft, and (2) turbulence and gravity wave phenomena using ground-based radar.

A number of laboratory kinetics and photochemical studies are being pursued. Key new data on NO_3, HO_2 and $ClONO_2$ reactions have been obtained. Improved rate measurements on the key reactions O+ClO and OH+HCl have been accomplished. Reaction rates which strongly affect the hydroxyl radical concentration, such as $OH+HNO_3$, $OH+HO_2NO_2$ and $OH+HO_2$, are now better known. A comprehensive program of spectroscopic studies in the ultraviolet, infrared and microwave regions is being carried out to support the field measurement program and to improve the accuracy of our calculations of the penetration of solar radiation through the atmosphere.

Development of general circulation models for both troposphere and stratosphere continues. Theoretical studies using 1- and 2-dimensional models continue to investigate the effects of adding chlorofluoromethanes, N_2O, CO_2, and other species to the atmosphere. The key effects are on abundance and distribution of ozone, and consequent changes in the thermal structure and dynamics of the upper atmosphere. The most recent assessment, detailed in the first portion of this report (Present State of Knowledge of the Upper Atmosphere: An Assessment Report) estimates that the release of fluorocarbons 11 and 12, at the 1977 rates in an otherwise unchanged atmosphere, will result if an ozone column decrease in the range of 3-5%. The calculated effect would be increased by about 10-30% by inclusion of effects of temperature feedback, and is sensitive to changes in N_2O, CH_4, and CO_2 concentrations. The models continue to predict fluorocarbon-related depletions near 40 km which are comparable in magnitude to those in previous reports. A doubling of CO_2 levels, as is estimated to occur by the year 2050, is predicted to decrease the potential fluorocarbon impact on ozone column by as much as one third by modifying the temperature of the stratosphere. Further, the assumption of a continued increase in CH_4 of 1.5% per year leads to the result that ozone decreases would not occur until the middle of the next century. Thus, the actual impact of fluorocarbon release is critically dependent on the assumptions made with regard to the fluxes of other atmospheric components. Current photochemical models predict that injections of NO_x at either 17 or 20 km, from a hypothetical fleet of supersonic aircraft, would result in a decrease in stratospheric column ozone, whereas injections at lower altitudes, from subsonic aircraft, would result in the production of ozone.

Increased emphasis is being placed on the analysis of satellite data sets (Nimbus 4, 6, 7, Stratospheric Aerosol and Gas Experiment (SAGE), and Solar Mesospheric Explorer (SME) and results of dynamics and multi-sensor balloon experiments. About 20 new investigations have been funded to interpret the considerable satellite data sets which are now generally available to the research community.

Satellite measurements provide a global-scale picture of the state of the upper atmosphere and its variations which is not feasible from measurement platforms such as balloons and aircraft. In view of this the Upper Atmosphere Research Program supports a variety of missions conducted from earth orbit. The complement of instruments currently aloft on Nimbus-7 continues to provide simultaneous global measurement of nitrous oxide, methane, water vapor, temperature, ozone profiles and total ozone column density. The SAGE satellite, which has now ceased operation, has provided an unprecedented amount of aerosol and ozone data in the lower stratosphere. These data have been validated and are being analyzed in detail. A second SAGE will be launched in 1984. The analyzed observations of trace species and temperature will be extremely useful as input to global models and for testing certain facets of our theories regarding the coupling between chemistry, dynamics and energetics.

The SME, launched in September 1981, is continuously monitoring ozone, water vapor, temperature, the incident solar spectral irradiance, and energetic particle radiation. This will provide an initial step in the validation of oxygen-hydrogen photochemical theory by actually observing the thermal and chemical response of the mesosphere to measured variations in the solar energy input.

These satellite missions each focus on a specific part of the upper atmospheric system and on measurements of a limited set of species in the different chemical cycles. The proposed Upper Atmosphere Research Satellite (UARS) mission, planned for flight in the late 1980's, will provide the first simultaneous measurements of stratospheric chlorine, nitrogen, hydrogen, and oxygen species coupled with measurements of dynamical parameters (e.g., winds) and energy inputs and losses. The complement of UARS experiments will be focused on global budgets of gases important in the ozone balance, on the dynamics and energetics of the upper atmosphere, and on couplings among these processes. The extensive UARS data base will allow extensive study of the mechanisms of atmospheric variability and the response of the upper atmosphere to changes in external factors such as solar activity.

The remainder of this document consists of research summaries provided by investigators associated with the research tasks and flight missions supported by the UARP in FY 1982 and FY 1983. The reports are ordered according to the major categories of field measurements, laboratory studies, theoretical studies and data analysis. Additional sections also deal with recent satellite measurements and sensor development.

I. FIELD MEASUREMENTS

A. BALLOON-BORNE IN-SITU MEASUREMENTS

B. BALLOON-BORNE REMOTE MEASUREMENTS

C. GROUND-BASED MEASUREMENTS

D. AIRCRAFT-BORNE MEASUREMENTS

E. ROCKET-BORNE MEASUREMENTS

F. BALLOON FACILITIES

G. INSTRUMENT DEVELOPMENT

H. CALIBRATION FACILITIES

A. BALLOON-BORNE IN-SITU MEASUREMENTS

ATMOSPHERIC RESEARCH SUMMARY

A. Measurement of Trace Stratospheric Constituents with a Balloon-Borne Laser Radar

B. Principal Investigator: Dr. William S. Heaps
NASA/Goddard Space Flight Center
Greenbelt, Maryland 20771

Co-Investigator: Dr. Thomas J. McGee

C. Hydroxyl radical is a key species to our understanding of stratospheric chemistry. It affects the destruction of ozone by chlorofluorocarbons and oxides of nitrogen enhancing the former and retarding the latter. Despite this importance it is present at very low concentrations and is therefore quite difficult to measure. The balloon lidar makes use of remote laser induced fluorescence to detect and measure the hydroxyl radical. In this process a laser beam is tuned to a precise wavelength which causes hydroxyl to fluoresce. The strength of this fluorescence is measured and the hydroxyl concentration is inferred from this measurement.

D. An earlier version of this instrument was destroyed after a successful flight when the gondola suffered a mechanical failure during parachute deployment. The instrument was rebuilt and flown in October of 1982. Although hydroxyl was measured on this flight the quality of data was poor as the new instrument suffered several engineering failures which degraded laser power and stability. These problems have been corrected and the instrument is scheduled to fly a second time in October 1983.

E. No journal publications have resulted from the new instrument to date but analysis of flight data from the first instrument was completed resulting in the following article:

Heaps, William S. and T. J. McGee, "Balloon-Borne LIDAR Measurements of Stratospheric Hydroxyl Radical", J. Geophys. Res., 88, 5281, 1983.

NASA SUMMARY

A. "Direct Measurement of Photolysis Rates of Stratospheric and Mesospheric Interest."

B. Dr. Donald H. Stedman, Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109 in process of transferring to the University of Denver, Denver, Colorado 80208.

C. Abstract

The photochemistry of the atmosphere is driven by the solar photolysis of various molecules. The rate of photolysis is a function of solar intensity and the molecular properties absorption cross section and quantum yield. Calculations of photolysis frequencies depend on an accurate knowledge of all three parameters. In view of probable inaccuracies in these calculations, the objective of this project is to measure these parameters directly using chemical actinometry, to compare the measurements to current models. A subsidiary objective is to devise and calibrate electronic photometers which will provide a cost effective surrogate measurement suitable for routine field use.

D. Progress and Results in 1982-1983

$j(NO_2)$

The automated $j(NO_2)$ detector has been used for further trophospheric measurements in conjunction with the calibrated photometer.

$j(O_3\text{-}O(^1D))$

The results of an extensive ground and aircraft tropospheric $j(O_3\text{-}O(^1D))$ study have been published. A newly designed instrument capable of automated ground level $(j(O_3))$ determinations has been run for twelve months. Correlation of observed parameters with solar zenith angle, temperature and ozone column are in preparation.

j(N_2O) and (NO)

After much effort a GC inlet system capable (occasionally!) of sampling ppm levels of N_2 has been perfected. Calibration tubes for j(N_2O) have been constructed and tested. Two of the sealed quartz tubes were flown in the stratosphere in 1982. Analysis indicated a readily measurable N_2 photolysis product consistent with modelled values. In 1983 thirteen of the quartz tubes were exposed in the stratosphere with various He/N_2O fill ratios to test for optical thickness effects. Since the GC system (and the remainder of funds in the grant) are being moved to the University of Denver, analysis has not yet been carried out. All investigators were impressed that only four of the thirteen tubes were broken by the shock of landing and some accidental subsequent dragging of the payload behind a wayward parachute.

j(O_2)

Laboratory tests have shown that our j(O_2) payload which uses an ozone detector provided by J. Horvath will be sensitive down to a j of as low as 10^{-11} s^{-1}. Based on these tests a balloon payload has been constructed and will be flown (in collaboration with D. Murcray) in late 1983.

Program: Upper Atmospheric Research

Research Task: In-Situ Measurements of Stratospheric Ozone
Current RTOP No.: 147-11-05-50

Investigator: Donald E. Robbins, PhD
NASA-Johnson Space Center
Houston, TX 77058

Research Objectives: Perform research to measure atmospheric ozone with the highest accuracy possible to aid in validating satellite measurements and testing models used to study the chemistry of stratospheric ozone.

Summary of Progress and Objectives:

Less than five years ago the best accuracies quoted for in-situ ozone measurements were in the range of 15 percent. Measurements of ozone vertical distributions are required within an accuracy of 3 to 5 percent to adequately assess the long-term stability of ozone. During 1982 and 1983 several improvements were made to the NASA-JSC ozone instrument that allow measurements of ozone with an accuracy within 3 percent at altitudes below 35 km. Although the instrument is capable of making measurements up to 45 km some questions about possible loss of ozone on the walls of the inlet line and absorption cell at higher altitudes have arisen. A task of assessing the magnitude of these losses has been initiated.

NASA-JSC has participated in two international balloon campaigns to assess accuracies of techniques used to measure species involved in ozone chemistry. We were the only group to provide in-situ measurements of ozone during the two flights of the Balloon Intercomparison Campaign (BIC). Those flights were made in September 1982 and June 1983. Data reduction has been completed. Analysis and comparison with results of the remote measurements techniques are in progress. Two flights were made during the Balloon Ozone Intercomparison Campaign (BOIC), one on a NASA-GSFC gondola on which five other groups made in-situ measurements. Data analysis and comparisons are in progress. The second flight of BOIC was on a University of Minnesota gondola that carried a mass spectrometer to measure the ozone profile. Analysis of data is in progress. Three of these balloon flights (the two of BOIC and BIC-II) were made within one month during the summer of 1983.

Preparations have been made to participate in the September 1983 campaign of the MAP/GLOBUS program in France. NASA-JSC will make two balloon flights as a part of that campaign and serve as the "transfer standard" to allow intercomparisons between the European campaign and the American BIC and BOIC campaigns.

Journal Publications:

Robbins, D.E., "NASA-JSC Measurements during 'la Campagne d'Intercomparaison d'ozonometres' Gap, France-June 1981", Planetary and Space Sciences, 1983.

Aimedieu, P., A. J. Krueger, D. E. Robbins and P. C. Simon, "Ozone Profile Intercomparison based on Simultaneous Observation between 20 and 40 km", Planetary and Space Science, 1983.

NEUTRAL CONSTITUENT MEASUREMENTS

IN THE STRATOSPHERE

Dr. Konrad Mauersberger, School of Physics and Astronomy
University of Minnesota, Minneapolis, MN 55455

Research Objectives: To obtain measurements of major and minor neutral constituents in the middle and upper stratosphere using a gas expansion system combined with a mass spectrometer. Mixing ratios of O_3, H_2O and CO_2 have been measured, including the isotopes of O_3 and CO_2. Further development of the experiment is in progress to permit the detection of ClO.

Summary of Progress and Results: The mass spectrometer-beam system was flown twice during the 1982/83 time period. Both flights were successful and resulted in mixing ratio profiles of ozone and its isotopes as well as other constituents. In both flights an enhancement of heavy ozone was found at high altitudes, exceeding the expected abundance of ${}^{16}O_2{}^{18}O$ by about 30%. The enhancement decreased toward lower altitudes, reaching the standard value below 30 km. Photochemical theory cannot explain, at the present time, the enrichment in heavy ozone.

The laboratory calibration system has been improved to permit the simulation of stratospheric pressures and temperatures. Ozone gas mixtures can be made with an absolute accuracy of better than ±2%. New calibration procedures for water vapor have been established. A well-known standard mixture of H_2O in N_2 is available. The mixing ratio of H_2O has been verified by NBS.

Laboratory tests are in progress to increase the sensitivity and dynamic range of the experiment. Adaption of a channel plate multiplier within the mass spectrometer will permit in future balloon flights the detection of ClO in the upper stratosphere.

Journal Publication:

K. Mauersberger, Mass Spectrometry in the Stratosphere, Adv. Space Res. 2, 287, 1983.

A. BALLOON-BORNE DIODE LASER MEASUREMENTS OF STRATOSPHERIC TRACE SPECIES

B. Principal Investigator: Dr. Christopher R. Webster
Co-Investigator: Dr. Robert T. Menzies
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

C. Abstract of Research Objectives

The Balloon Laser In-Situ Sensor (BLISS) task has as its primary objective the collection of reliable data on the concentrations, distributions, and variabilities of the minor and trace species in the stratosphere. These data are to be used by modelers and dynamicists to assess and predict the effects of change in the chemical content of the upper atmosphere due to anthropogenic activity.

The BLISS instrument uses tunable diode lasers (TDLs) to measure the absorption due to selected species between the balloon gondola and a lowered retroreflector which defines a 1-km absorption path. The TDL beam in use is stabilized onto the lowered retroreflector by use of an optical tracking system. Several species can be measured simultaneously to the 0.1 ppbv level in sensitivity, throughout a diurnal cycle, and with the additional possibility of altitude profiling.

Two balloon flights of BLISS are planned for 83/84 with the goal of measuring key species in the odd-nitrogen family and their relative abundances throughout a diurnal cycle. These include NO_2, NO, HNO_3, and HO_2NO_2. The species O_3 and H_2O will also be measured.

D. Summary of Progress and Results

The BLISS instrument is a fully-integrated instrument which has successfully completed final testing before its first flight in September 1983, when two TDLs will measure NO_2, NO, and possibly H_2O and O_3 in the 30-40 km altitude region with a 0.5 km vertical resolution.

The ground support electronics, comprising a master console and three separate video monitors, have been assembled and programmed to handle the 128 downlinked data words. An HP9836 computer has also been interfaced to the downlink data side to make real-time recordings of spectral traces for the reference, power, and derivative signal channels, downlinked every 0.125 seconds. This addition allows ten 16-second consecutive spectral scans to be averaged for improved signal-to-noise ratio.

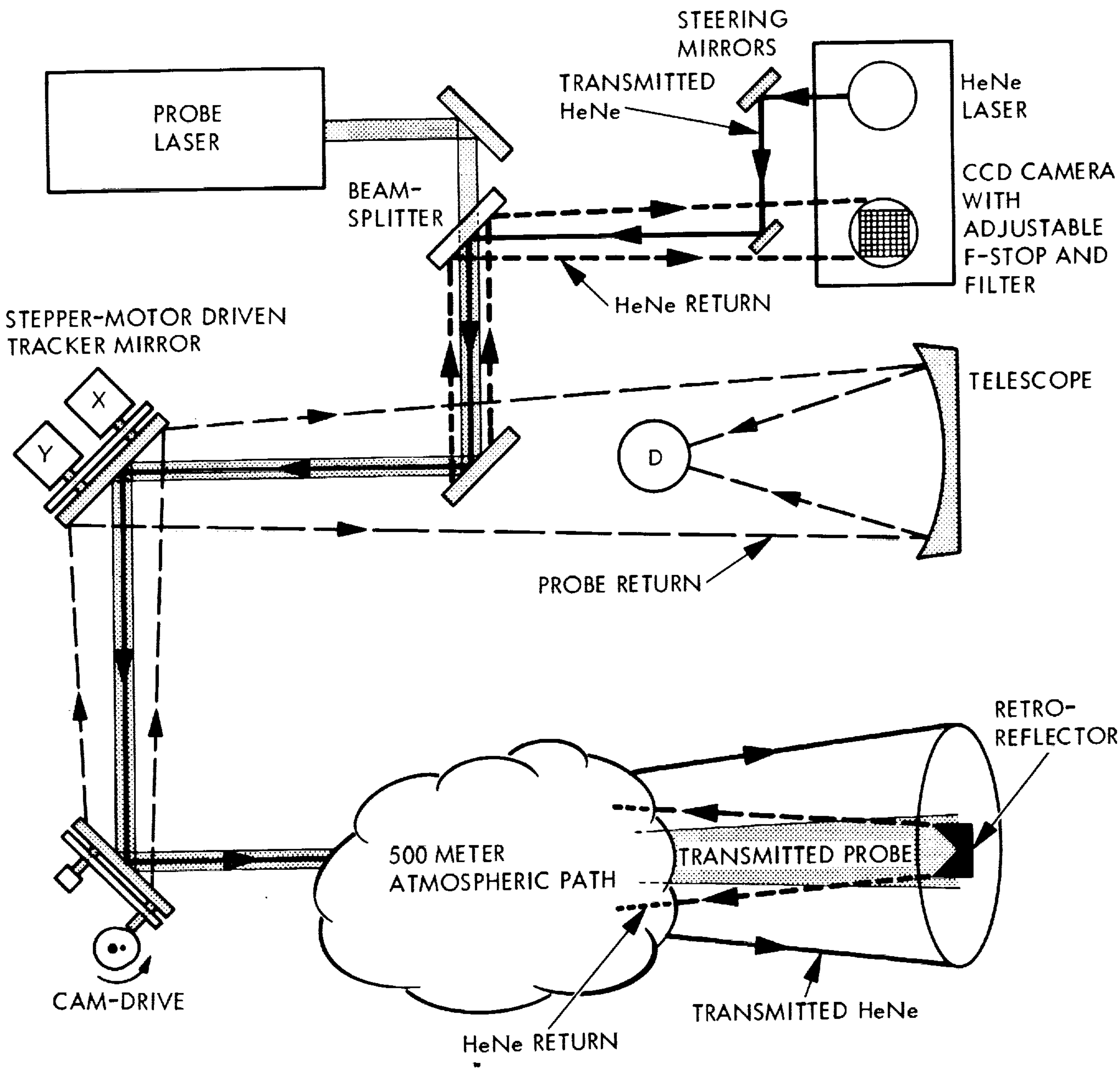
Long-path testing using a retroreflector at 500 meters has established the high performance and reliability of the tracking system, where an intermediate sinusoidally-driven mirror has simulated the pendulum motion expected in flight, with retroreflector angular velocities of up to 2.5 mrad s^{-1}.

At shorter pathlengths (retro at 70 meters) while tracking with the "moving" retro, an absorptance sensitivity of 1 in 10^4 (corresponding to 0.1 ppbv for NO_2 with a retro at 500 meters) has been demonstrated. The atmospheric turbulence and scintillation present in these tropospheric tests will not be such a problem at stratospheric altitudes.

E. Journal Publications

1. "Balloon-borne Diode Laser Absorption Spectrometer for Measurements of Stratospheric Trace Species," R. T. Menzies, C. R. Webster, and E. D. Hinkley, Applied Optics, September (1983).
2. "Infrared Laser Optogalvanic Spectroscopy of Molecules," C. R. Webster and R. T. Menzies, J. Chem. Phys., 78, 2121 (1983).
3. "Optogalvanic Wavelength Calibration for Laser Monitoring of Reactive Atmospheric Species," C. R. Webster, Applied Optics, 21, 2298 (1982).

BLISS OPTICAL TRACKING SYSTEM



TITLE: A FIELD MEASUREMENT PROGRAM INVESTIGATING THE CONCENTRATION OF FREE RADICALS IN THE STRATOSPHERE: THE IN SITU DETECTION OF OH, HO_2, H_2O, $O(^3P)$, O_3, Cℓ, CℓO AND NO.

INVESTIGATOR AND INSTITUTION: James G. Anderson, Harvard University

SUMMARY OF PROGRESS AND RESULTS:

During the 1982-83 period two major systems were completed and successfully launched. The first was the balloon-borne stratospheric Reel Down/Reel Up experiment depicted in Figure 1. This new approach to in situ measurements in the stratosphere employs a winching platform, suspended below the balloon at or near the stratopause, which contains ~ 20 km of kevlar cable capable of suspending a cluster of instruments. By command from the ground, the winch and associated line handling devices lowers the instrument array the desired distance, at the desired descent velocity, and then draws the instrument back up to a "docking" location below the winch system. The first launch of the stratospheric Reel Down experiment had three principle objectives: (1) determine the dynamical behavior of a system comprised of a winching platform suspended below a balloon at an altitude of 40 km from which a cluster of instruments is lowered on a kevlar filament 12 km in length; (2) diagnose the flow conditions through the instrument core using a newly developed flow tube geometry and blower system to prevent "tripping" of the flow at the instrument nose resulting from shear in stratospheric wind fields; (3) test the newly designed winching mechanism for mechanical and/or electronic flaws. On September 15, 1982 the first launch of the system took place from Palestine, Texas. The balloon-winch-suspended payload ascended to 133,000 ft. Following ascent, the pin locking the suspended payload to the winch was pulled and the instrument cluster was lowered 12 km at 7.5 m/sec. The experiment cluster was then drawn successfully back to the winch platform. Several critical points were demonstrated: (1) The entire system was exceedingly stable. There was a virtual absence of horizontal and rotational motion and the load cells at both ends of the line showed less than 2 percent deviation from 1 g acceleration. (2) The redundant resonance fluorescence instruments on the suspended payload operated perfectly and the impeller-controlled flow exhibited simple laminar flow through the instrument core.

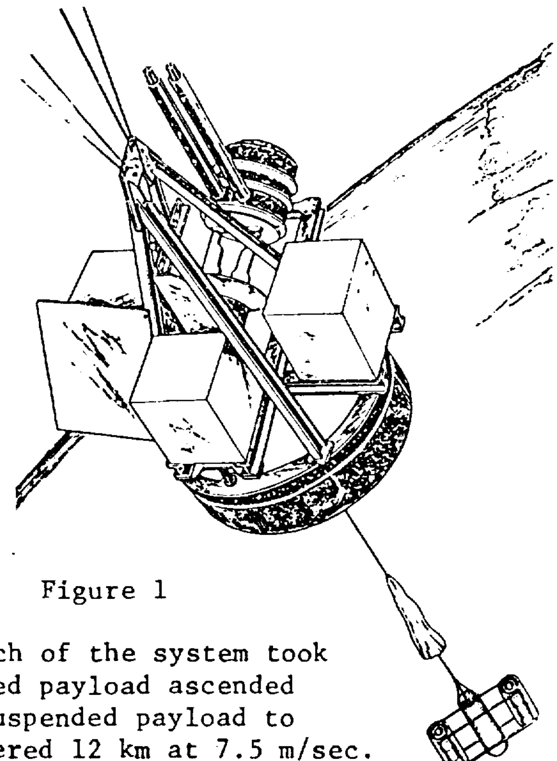
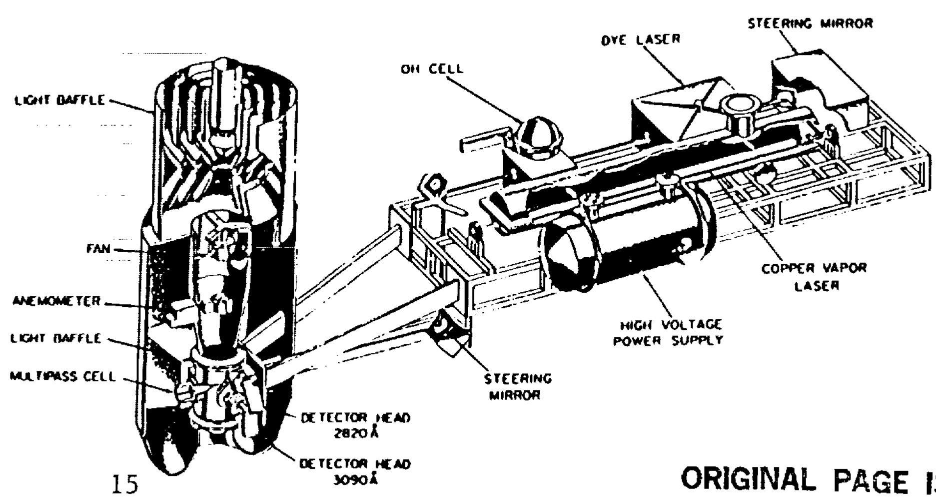


Figure 1

The second major system to be completed and successfully flown was the copper vapor laser designed for the detection of OH and HO_2 in the stratosphere. That system, summarized in Figure 2, consist of a copper vapor laser pumped dye laser, an on-board OH cell to directly detect fluorescence from OH, a flow system to contain and control the stratospheric air sample, optics to



control and amplify the laser beam, a high voltage power supply to drive the copper vapor laser and a telemetry system to relay the data to the launch site. The system was successfully launched on September 22, 1983 from Palestine, Texas. All systems worked very well, demonstrating a factor of 1000 gain in sensitivity over previous in situ OH detection methods.

Two other major instrument design and development efforts were successfully concluded. The first resulted in the completion of a cryogenically cooled H_2O frequent fluorescence experiment which will provide the first high resolution in situ H_2O data obtained at midday (in conjunction with the OH measurements). This is shown in Figure 3. The second is a significantly improved Cℓ/CℓO experiment which will, when used with the Reel Down experiment, provide x 100 gain in sensitivity from those previously used. This is shown below in Figure 4.

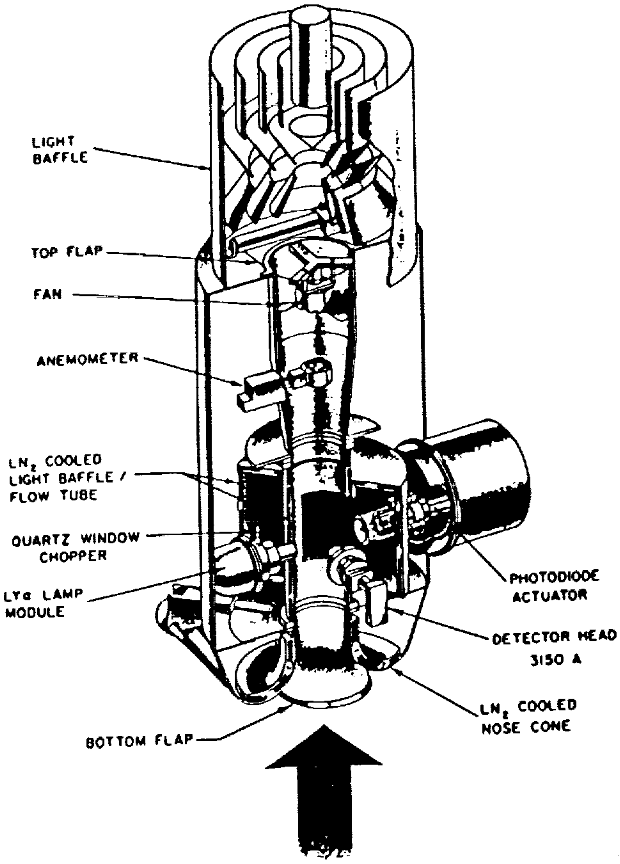


Figure 3

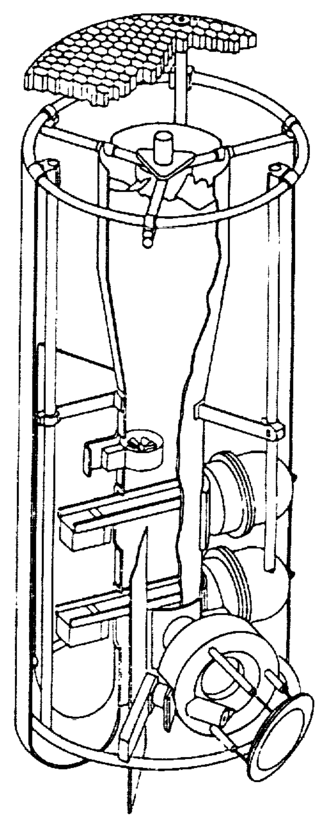


Figure 4

Publications:

1. Anderson, J.G., The Chemistry of Stratospheric Chlorine, Chapter 6, Stratospheric Ozone and Man, CRC Press, 1982.
2. Stimpfle, R.M. and J.G. Anderson, Tropospheric OH Observations: Application of the High Repetition Rate Atomic Copper Vapor Laser. Second Symposium on the Composition of the Non Urban Troposphere 1, 330, 1982.
3. Lapson, L.B., J. Demusz, R.M. Stipfle and J.G. Anderson, Free Radicals in the Stratosphere: Copper Vapor Laser Detection of OH. Applied Optics, in preparation.
4. Anderson, J.G., N.L. Hazen, S.P. Rowe, E. Weinstock and J.P. Schwab, In Situ Detection of Free Radicals in the Stratosphere: A New Approach. Science, in preparation.
5. Hazen, N.L. and J.G. Anderson, Reel Down: A Balloon Borne Winch System for Stratospheric Sounding from Above, American Institute of Aeronautics and Astronautics, Aerospace Sciences, in preparation.

Project Report for 1982-1983

Title: "Development of Reference Calibration Standards for Selected Halocarbons and Nitrous Oxide." (NASA Contract #15,032)

Principal Investigator: James Elkins
Gas & Particulate Science Division
Center for Analytical Chemistry
National Bureau of Standards
Washington, DC 20234

Abstract of Research Objectives: The objective of this research is the development of absolute calibration gas standards for nitrous oxide (N_2O), and halocarbons F-11 (CCl_3F) and F-12 (CCl_2F_2). Absolute gas standards are needed to assess analytical uncertainties in the monitoring measurements of temporal and spatial distributions of the halocarbons and nitrous oxide in the atmosphere. Gas standard mixtures containing N_2O, F-11 and F-12 are currently under development by the National Bureau of Standards as "Standard Reference Materials" (SRM's).

Summary of Progress: Three sets of gravimetric gas standards for nitrous oxide, and halocarbons F-11 and F-12 were prepared. The concentrations of the gravimetric standards were verified by two independent techniques: gas chromatography and infrared absorption spectroscopy. After the gravimetric standards were verified, a group of atmospheric gas mixtures were obtained commercially at three different concentrations, and were compared to the original set of gravimetric standards. These standards will be released as SRM's following verification of the stability of the gas mixtures.

The infrared band strengths of halocarbons F-11 and F-12, and methyl chloride were measured by a Fourier transform infrared (FT-IR) spectrometer at a resolution of 0.06 cm^{-1} as part of our research program to investigate the possibility of IR measurement of halocarbons at ambient concentrations. Our results for the strengths of F-11 and F-12 would indicate a stronger IR absorption than previous results taken at lower instrumental resolution.

Publications:

Kagann, R.H., J.W. Elkins, and R.L. Sams, "Absolute Band Strengths of Halocarbons F-11 and F-12 in the 8 - 16 μm Region", Journal of Geophysical Research, 88 1427-1432 (1983).

Elkins, J.W., R.H. Kagann, and R.L. Sams, "Infrared Band Strengths for Methyl Chloride in the Regions of Atmospheric Interest", Journal of Molecular Spectroscopy, submitted for publication (1983).

15 Sept 83

NASA PROGRESS REPORT FOR 1982 and 1983

A. Title of Research Task: MEASUREMENTS OF THE VERTICAL PROFILES OF TOTAL CHLORINE AND TOTAL BROMINE IN THE STRATOSPHERE

(Proposal No. 742-UA-251; Interagency Agreement No. W-15,437)

B. Investigators and Institutions:

Walter W. Berg, Ph.D.
Group Leader, Global Halogen Project
National Center for Atmospheric Research
P.O. Box 3000
Boulder, CO 80307

C. Abstract of Research Objectives:

The scientific objectives of this research effort are twofold: (1) to provide a measured upper limit, as a function of altitude, to the total amount of chlorine and bromine available for potential catalytic destruction of stratospheric ozone, and (2) to explore the nature of any diurnal variability in the particulate and gas phase levels of chlorine and bromine in order to examine any chlorine/bromine heterogeneous behavior. Two long-duration, balloon-borne sampling missions are planned in which total chlorine, bromine, and iodine in both the gaseous and particulate phase will be determined at 36 ± 2 km and 23 ± 2 km.

D. Summary of Progress and Results (1982 and 1983):

As a result of our October 1981 balloon flight (payload free-fell 3 km at termination and was totally destroyed) the 1982 and 1983 period was used to build a completely new payload. Design of the multi-experiment platform was initiated in January 1982 and construction was started by June 1982. The payload was completed in April 1983. The period May to December 1983 was used to rigorously test the fully automated payload under stratospheric conditions. The stand-alone communications link between the payload and our ground support trailer (in which a UART is connected to a modem for a 1200 BAUD full duplex link via UHF radio to a trailer based HP-85 computer) was tested in a low pressure and temperature regime. Cryogenic-trapping system tests were completed in August 1983 with a twenty-one pump unit. Tests on our CMOS-based flight computer were completed in September. During this period, two weeks of tests were also performed at the Holloman AFB stratospheric chamber facility on the mission-ready payload under cold-soaked conditions (-65°C, in the 20 to 40 km altitude range). The payload is now flight ready for the Spring 1984 turn-around period.

Approximately 70% of the data was recovered from the 1981 payload destruction and worked into publishable form early 1982. We plan, however, to wait for a second corroborating flight by the new payload before releasing this data. As a result, no results were published during 1982 and 1983 from this research effort.

E. Journal Publications: None

SUMMARY OF PROGRESS AND RESULTS FOR CY1982 AND CY1983

A. TASK

DASIBI measurement of ozone profile and column content.

B. INVESTIGATOR AND INSTITUTION

John E. Ainsworth, Jr.
NASA/Goddard Space Flight Center
Code 963
Greenbelt, Maryland 20771
(301) 344-8738

C. RESEARCH OBJECTIVES

To reduce the error in the in-situ measurements of ozone concentration profiles from balloons to the extent required for their use in the verification of satellite measurements of the long term drift in the total global ozone.

D. RESULTS AND PROGRESS

In CY1982 we began the design and development of two new UV ozone photometers to replace our previous instrument, destroyed during a hard landing. The two new instruments were flown with partial success on October 25, 1982. At this stage of their development and testing the instruments demonstrated for the first time that it is possible to obtain good agreement between two "identical" ozone measuring instruments flown on the same balloon. They obtained measurements which agreed to within ± 1.5% in the region from 26 to 33 km and showed matching features in the ozone vertical structure with amplitudes of from 0.5 to 1%.

In CY1983 we have continued the development and testing of the two new UV ozone photometers. The two instruments were flown again on July 10, 1983 (BOIC #1), but due to the fact that the balloon reached float at 26 km, rather than 40 km, our principal achievement on this flight was limited to a demonstration that highly accurate temperature measurements can be obtained from 0 to 26 km and that modulation of these temperatures by the gondola provides essential flight information. However, measurements obtained by Robbins from the second BOIC #1 gondola on July 18, 1983 succeeded in verifying our laboratory measurements and flight comparisons that indicated that instrument wall-loss is inversely related to atmospheric pressure and that a substantial correction can be required at 40 km.

E. PUBLICATION

"Correction of Dasibi ozone measurements for the weak-line contribution", J. R. Hagemeyer and J. E. Ainsworth, Rev. Sci. Instrum., 53, July 1982.

ECC Sonde Ozone Measurements During BOIC

W. D. Komhyr, A. N. Chopra, S. J. Oltmans

NOAA Air Resources Laboratories, Boulder, Colorado 80303

Research Objectives

During BOIC, the performance of Komhyr ECC (electrochemical concentration cell) balloon-borne ozonesondes was evaluated relative to Brewer bubbler sondes, as well as relative to more sophisticated ozone measuring instrumentation such as the U.V. ozone photometer of Ainsworth, Proffitt and Robbins. Of particular interest is reliability of ozone data provided by the ECC sondes in the region of the stratosphere above the primary ozone maximum to 40 km altitude. Results of the instrument intercomparisons should provide information on whether ECC sondes can be usefully employed in providing comparison ozone data for satellite ozone observations.

Summary of Progress

During 19 June through 7 July 1983, a series of 16 triplet balloon ozonesonde flights were made at the National Balloon Facility, Palestine, Texas, to compare the performance of several varieties of Komhyr ECC ozonesondes and Brewer-Most bubbler sondes. ECC instruments flown were older 3A sondes used in the past, and newer type 4A sondes designed for operation to 40 km altitude. Data from the soundings have been processed and forwarded to the BOIC Project Manager, E. Hilsenrath.

Six ECC sondes were flown at Palestine, Texas, on the main BOIC instrument package on 10 July 1983. Data were obtained to near the altitude of the atmospheric ozone maximum. A preliminary comparison of processed data has indicated good agreement in results given by ECC sondes and the U.V. photometer instruments of Proffitt and Robbins.

An additional eight ECC sondes were flown from Palestine, Texas, on the instrumented BOIC gondola on 24 October 1983. As of 7 November 1983, data tapes from the flights were unavailable for processing.

Extensive laboratory and environmental chamber tests have been conducted on the ECC sondes to assess sonde pump efficiencies to 3 mb altitude, pump temperature coefficients, sensor solution evaporation rates, and ozone loss through the sensors at high altitude. Eight of the sensors flown were calibrated relative to the NBS standard ozone source of A. N. Bass.

During the campaign, total ozone and Umkehr observations were made at Palestine. The Umkehr data are being processed at the World Ozone Data Center in Canada.

This work has been supported in part by NASA.

B. BALLOON-BORNE REMOTE MEASUREMENTS

TITLE OF RESEARCH TASK: Airborne Measurements of Minor Constituents of the Stratosphere.

INVESTIGATORS: David G. Murcray, Physics Department, University of Denver
Frank J. Murcray, Physics Department, University of Denver
Aaron Goldman, Physics Department, University of Denver

ABSTRACT OF RESEARCH OBJECTIVES:

The objective of this program is to obtain data concerning the concentration and altitude distribution of various constituents of interest in the photochemistry of the ozone layer. Data pertinent to this objective are to be obtained using instruments which can be carried to high altitudes by balloons or the NASA U-2 aircraft. Major emphasis in this program has been placed on using infrared techniques for the measurements of constituents, however water vapor data have also been obtained using a frost point hygrometer system.

SUMMARY OF PROGRESS AND RESULTS:

During the period covered by this report, major emphasis has been placed on participation in the Balloon Intercomparison Campaign (BIC). This campaign had as its objective the simultaneous measurement of several chemical constituents by numerous remote sensing instruments. In order to achieve this objective, the instruments were combined into four gondolas. These four gondolas were to be launched as close together in time as possible so the various instruments would obtain data in the same air mass. Our participation in this program required that we integrate our balloon-borne solar interferometer system into a gondola constructed by the National Physical Laboratory (NPL) of England; our atmospheric emission spectrometer was integrated into a gondola constructed by Jet Propulsion Laboratory (JPL). Both of these instruments are capable of measuring a number of constituents of interest in the photochemistry of the ozone layer. The particular constituents measured depend on the wave length region scanned. For these flights primary emphasis was placed on getting data on $HC\ell$ and HNO_3. Details of the BIC field program are given in other reports in this volume and need not be repeated here. The JPL gondola with our atmospheric emission spectrometer set to scan the wavelength regions from 6.5 μm to 9.0 μm and from 9.0 μm to 13.5 μm was flown on September 22, 1982. The instrument operated properly and data were obtained throughout the flight. The instrument was recovered without incident or damage. The NPL gondola was also launched on September 22, however the balloon was faulty and the flight had to be terminated shortly after launch. The payload was recovered, renovated and launched again on October 5,

1982. Some problems were encountered with the PCM telemetry on this flight, but it was possible to recover the data. The system overheated and had to be turned off until just before sunset. At that time the instrument was turned on and was operating properly until the solar zenith angle was approximately 90°. At this point the gondola orienting system was disturbed and the system did not reacquire the sun.

For the spring 1983 BIC, the emission system was set to scan from 9.0 μm to 13.5 μm and from 17 μm to 28 μm. The JPL gondola with this unit was launched June 17 and terminated June 18. The flight went very well and our unit operated properly throughout the flight. Primary emphasis of this flight was again on HNO_3. The change in wavelength on the second channel to the 17 μm to 28 μm was made to obtain data on H_2O.

Our solar interferometer was configured the same as for the fall flight, and was again flown on the NPL gondola which was launched June 20. Our instrument operated properly on this flight and data were obtained during the sunset transition with the unit. This gondola was dragged by the parachute and our unit suffered considerable damage to the solar tracker. The interferometer was packed with dirt but suffered no physical damage.

Data obtained on these flights will be analyzed and the various profiles compared with those of other investigators. It is expected that the results will be published as a joint paper or series of papers with the other investigators in the program.

JOURNAL PUBLICATIONS:

Rinsland, C.P., M.A.H. Smith, R.K. Seals, Jr., A. Goldman, F.J. Murcray, D.G. Murcray, J.C. Larsen and P.L. Rarig, "Stratospheric Measurements Collision-Induced Absorption by Molecular Oxygen," J. Geophys. Rev., 87, 3119-3122, 1982.

Goldman, A., R.D. Blatherwick, F.J. Murcray, J.W. VanAllen, F.H. Murcray and D.G. Murcray, "Atlas of Stratospheric IR Absorption Spectra," Appl. Opt., 21, 1163-1164, 1982.

Goldman, A., R.D. Blatherwick, F.J. Murcray, J.W. VanAllen, F.H. Murcray and D.G. Murcray, "New Atlas of Stratospheric IR Absorption Spectra--Vol. I and II," Dept. of Physics, Univ. of Denver, February 1982.

Rinsland, C.P., A. Goldman, F.J. Murcray, D.G. Murcray, M.A.H. Smith, R.K. Seals, Jr., J.C. Larsen and P.L. Rinsland, "Stratospheric N_2O Mixing Ratio Profile from High Resolution Balloon-Borne Solar Absorption Spectra and Laboratory Spectra Near 1880 cm^{-1}," Appl. Opt., 21, 4351-4355, 1982.

Murcray, D.G., F.J. Murcray, A. Goldman, F.H. Murcray and J.J. Kosters, "Balloon-Borne Sensing of Stratospheric Chemical Constituents, " Appl. Opt., 22, 2629-2240, 1983.

Goldman, A., D.G. Murcray, D.L. Lambert and J.F. Dominy, "The Pure Rotation Spectrum of the Hydroxyl Radical and the Solar Oxygen Abundance," Mon. Not. R. Astr. Soc., 203, 767-776, 1983.

A. Research Task: Thermal Emission Spectroscopy of the Middle Atmosphere

B. Investigators:

Virgil G. Kunde
John J. Hillman
Barney J. Conrath
Rudolf A. Hanel
Jay R. Herman
Donald E. Jennings
William C. Maguire

Goddard Space Flight Center
Greenbelt, MD 20771

John C. Gille
William G. Mankin
Michael T. Coffey

National Center for Atmospheric Research
P. O. Box 3000
Boulder, CO 80307

Mian M. Abbas
Department of Physics and Atmospheric Science
Drexel University
Philadelphia, PA 19104

C. Research Objectives: The general objective of this research is to obtain simultaneous measurements of the vertical distributions of stratospheric ozone and several trace constituents that can contribute to its destruction (HO_X: H_2O, H_2O_2; NO_X: N_2O, NO, NO_2, HNO_3; CL_X: CF_2CL_2, $CFCl_3$, CCl_4, ClO). Additional species, such as HO_2, HO_2NO_2, N_2O_5, CH_3Cl, $ClONO_2$, and HOCl, which have not been detected previously by remote sensing will also be measured, provided they are present at the abundance levels predicted by current models. Data will be collected during a complete diurnal cycle in order to test our present understanding of ozone chemistry and its associated catalytic cycles. High spectral resolution measurements of the thermal emission of the limb will be obtained from a balloon-borne platform. The instrumentation employed is a liquid nitrogen cooled Michelson interferometer-spectrometer (SIRIS), covering the mid-infrared range. Cryogenic cooling combined with the use of extrinsic silicon photoconductor detectors allows the detection of weak emission features of stratospheric gaseous species.

D. Programs and Results: The SIRIS instrumentation is now fully integrated with the balloon gondola, along with the PCM telemetry system, and has been thoroughly tested with the instrument at cryogenic temperatures. The experiment meets all major technical requirements, environmental testing has been performed in September 1983, and the instrument is at Palestine, Texas for its initial balloon launch in October 1983.

E. Journal Publications: (1) Herman, J. R. and J. E. Mentall, "The Direct and Scattered Solar Flux in the Upper Stratosphere", J. Geophys. Res., 87, 1319-1330 (1982). (2) Aikin, A. C., J. R. Herman, E. J. Maier, and C. J. McQuillan, "Atmospheric Chemistry of Ethane and Ethylene", J. Geophys. Res., 87, 3105-3118 (1982). (3) Herman, J. R. and J. E. Mentall, "O_2 Absorption Cross Sections (187-225 nm) from Stratospheric Solar Flux Measurements", J. Geophys. Res., 87, 8967-8975 (1982).

Summary for 1982 and 1983

Title: Measurement of HO_2 and Other Trace Gases in the Stratosphere Using a High Resolution Far-Infrared Spectrometer at 28 km

Investigators: Wesley A. Traub, Smithsonian Astrophysical Observatory
Kelly V. Chance, Smithsonian Astrophysical Observatory
Stephen C. Wofsy, Harvard University

Abstract: Our scientific objectives are to detect and to accurately measure, in the stratosphere, the vertical distribution of molecules with far-infrared spectral features which are of key importance to stratospheric chemistry and to use these results to test current model predictions. We do this by remotely sensing the thermal infrared emission spectrum of the stratosphere near the limb, followed by computer modeling techniques to synthesize corresponding theoretical spectra. The broadband nature of the measurements allows us to determine all spectral features simultaneously; furthermore, since we measure in emission, we are able to measure throughout the full diurnal cycle. We currently measure the complete spectrum from about 80 to 220 cm^{-1} with an unapodized step size of 0.032 cm^{-1}. In addition to many tens of lines of H_2O, O_3, and O_2 we measure 4 lines of HCl, 2 lines of HF, and 12 lines of OH. At lower signal-to-noise ratio we also have available in our spectral region, but have not yet positively identified, 4 features due to HO_2, 3 features from H_2O_2, and 4 features from HOCl. Two recent successful balloon flights have yielded a large number of high-quality spectra which are currently being analyzed. Future plans include rebuilding the spectrometer with up to 8 times higher resolution, and nearly 3 times greater sensitivity to typically sharp stratospheric spectral lines.

Summary of Progress and Results: As part of our overall stratospheric program, we used our flight spectrometer to make laboratory measurements of chlorine nitrate ($ClONO_2$) and hypochlorous acid (HOCl). We found that the far-infrared torsional bands of $ClONO_2$ would produce a signal on the order of 10^{-4} of a blackbody in the stratosphere at an abundance of 1 ppbv, which unfortunately is a factor of about 10 below our detection threshold; we are currently pursuing the possibility of searching for vibrational transition in the neighborhood of 500 cm^{-1}, outside our present band. We also measured in the laboratory five Q-branches in the rotational spectrum of HOCl, and will use this data to search for stratospheric HOCl in our flight spectra.

In 1982 we built a small (14 cm), dedicated telescope for use with our spectrometer. The telescope system incorporates a single-axis stabilized platform which is controlled by the combination of an inclinometer, for long-term absolute gravity direction reference, and a rate-integrating gyro, for short-term pendulum motion information. The overall pointing accuracy of the telescope is well within ± 0.02 degrees, or about ± 0.15 km at the horizon. The telescope is highly baffled in order to produce a 3 km field of view, near the tangent height. Significant improvements to the spectrometer included increasing the reliability of the laser electronics, and repositioning the laser probe beam so as to eliminate weak interferences from spectral ghosts.

We had 2 highly successful balloon flights from Palestine, Texas, both in 1983. The first flight was primarily a test of the new telescope system, which worked quite well during most of the flight. The highlight, however, was the first detection of 12 far-infrared lines of the OH radical. The second flight was made as part of the Balloon Intercomparison Campaign (BIC-II); during the ascent and 13 hours at float, our instruments worked flawlessly, allowing us to obtain over 1600 spectra. The measurements cover nearly one-half of a diurnal cycle, roughly divided between afternoon and evening. At the end of the flight all instruments were unfortunately destroyed when the gondola free-fell from approximately 33 km. The analysis of data from these flights is currently underway, and will continue for about 2 years.

We currently hope to rebuild the spectrometer and telescope in order to continue our measurements of OH and the other species mentioned above. This will allow us to track abundance variations on diurnal, seasonal, and year-to-year scales, as well as, possibly, geographical variations. The new spectrometer will have up to 8 times enhanced spectral resolution, which will improve our sensitivity to narrow lines, and also greatly reduce the problems of analysis which are caused by line blending.

Publications:

Q branches in the rotational spectrum of HOCl (K. V. Chance and W. A. Traub). J. Quant. Spectrosc. Radiat. Transfer **29**, pp. 81-84, 1982.

Use of a Fourier transform spectrometer on a balloon-borne telescope and at the Multiple Mirror Telescope (MMT) (W. A. Traub, K. V. Chance, J. C. Brasunas, J. M. Vrtilek, and N. P. Carleton). Proc. S.P.I.E., Instrumentation in Astronomy IV **331**, pp. 208-218, 1982.

The torsional spectrum of chlorine nitrate (K. V. Chance and W. A. Traub). Journ. Molecular Spectroscopy, **92**, pp. 306-312, 1982.

A Stabilized platform for balloon-borne remote sensing (L. M. Coyle, G. U. Nystrom, J. Bortz, B. Nagy, K. V. Chance, and W. A. Traub) to be submitted, 1983.

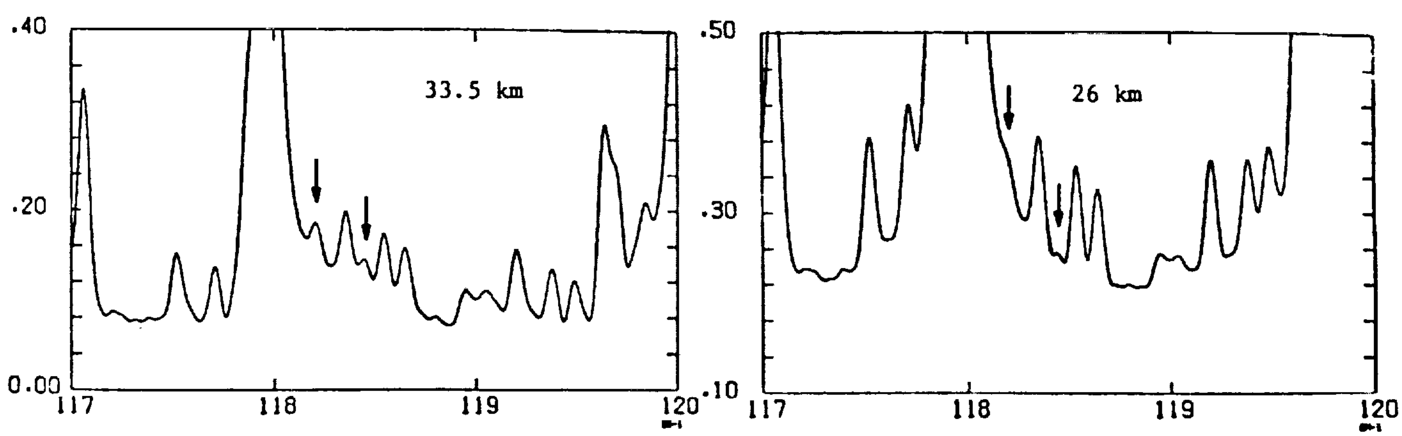


Figure 1. The two components of OH $^2\Pi_{3/2}$ J = 5/2 → 7/2 are indicated by arrows. Both spectra were taken from a balloon platform at 36 km. The tangent height for each spectrum is indicated. Other spectra in this flight cover the range from 21 km to roughly 42 km.

UV SOLAR FLUX IN THE STRATOSPHERE

J. E. Mentall and J. R. Herman
NASA/Goddard Space Flight Center
Laboratory for Planetary Atmospheres
Greenbelt, Maryland 20771

Abstract:

Measurements are made of both the direct and scattered components of the solar flux over the wavelength range 180-350 nm. These are made from a balloon-borne platform so that data is obtained within the stratosphere between 20 and 40 km. Data are used to test the results of radiative transfer calculations, obtain absorption cross sections from in-situ measurements, determine ozone profiles for comparison with profiles obtained by other techniques, and provide fundamental radiation field data needed to interpret results from complex, multi-instrument balloon missions.

Summary of Progress and Results:

Ascent data obtained on the Solar Absorption Balloon Experiment (SABE-3) on April 15, 1981 allowed the first direct calculations of the absorption cross sections to be obtained for the O_2 Herzberg continuum between 200 and 220 nm. Radiation in this region of the spectrum penetrates to the base of the stratosphere where it plays a key role in the photochemistry. Measurements of these cross sections are difficult because of the small size of the cross sections (10^{-23} cm^2) and their known pressure dependence. This problem is dealt with in the laboratory by making measurements at high pressure and extrapolating to zero pressure. A wide range of values have been reported in the literature but data from SABE-3 show that the best measurements are those reported by Shardanand and Rao and that the true cross sections are likely to be 30% lower. A similar analysis of the 220 and 330 nm region of the spectrum demonstrated that the ozone absorption cross section of Inn and Tanaka and of Bass and Paur used with the temperature dependence of Vigroux are accurate to at least 3%.

Ozone densities obtained from the SABE-3 flight were compared with those obtained by the GSFC Dasibi experiment. Agreement between the two instruments was within 5%. A paper comparing the ozone profiles obtained by some of the instruments flown on SABE-2 and SABE-3 is in preparation. A simplified spectrometer experiment for measuring ozone profiles has been constructed and will be flown as part of the Balloon Ozone Intercomparison Campaign (BOIC) in October 1983.

An experiment for making simultaneous measurements of the direct and scattered UV flux was designed and flown as part of the Balloon Intercomparison Campaign on June 20, 1983 from Palestine, Texas. This experiment was designed to give the total UV radiation field in support of the experiments measuring chemical within the stratosphere. Good data was obtained at float altitude but near sunset the direct solar irradiance instrument stopped giving reliable data due to overheating. Had the experiment been recovered after the flight, some of the sunset data could have recovered through laboratory testing of the instrument. Unfortunately, the parachute recovery system failed and the entire gondola was destroyed. This payload is being rebuilt and flown in the Summer of 1984. The purpose of this flight will be to determine accurate absorption cross sections in the Herzberg continuum and to study radiative transport through sunset.

Publications:

"The Direct and Scattered Solar Flux within the Stratosphere", J. R. Herman and J. E. Mentall, J. Geophys. Res., 87, 1319, 1982.

"O_2 Absorption Cross Sections (187-225 nm) from the Stratospheric Solar Flux Measurements", J. R. Herman and J. E. Mentall, J. Geophys. Res., 87, 8967, 1982.

Material for January 1984 NASA Upper Atmosphere Report

A. <u>Title of Research Task</u>

Upper Atmospheric Measurements with Balloon-Borne Millimeter and Submillimeter Heterodyne Radiometers

B. <u>Investigators and Institutions</u>

Dr. J. W. Waters (P.I.)
Dr. R. F. Jarnot
Dr. H. M. Pickett
Dr. W. J. Wilson
Dr. P. Zimmermann

C. <u>Research Objectives</u>

This investigation develops microwave techniques at mm and submm wavelengths for upper atmospheric measurements. Such techniques are well suited for observing thermal emission and can measure a variety of species important in upper atmospheric chemistry, as well as temperature and winds which are important for understanding dynamics. One important goal of the investigation is to determine the capabilities and limitations of these techniques so they can be used efficiently in NASA's overall upper atmospheric research program. Measurements already made from ground, aircraft, and balloon platforms include O_3 (15-80 km), $C\ell O$ (20-40 km), H_2O (30-80 km), N_2O (30-40 km), CO (50-80 km), and tentatively, H_2O_2 (3035 km). Advances in technology will allow many more species to be measured including atomic O, $HC\ell$, $HOC\ell$, HO_2, NO_2, NO, and others. This program has led to a Microwave Limb Sounder experiment for the Upper Atmosphere Research Satellite now under study.

D. <u>Progress</u>

The Balloon Microwave Limb Sounder (BMLS) was flown as part of the NASA Balloon Intercomparison Campaigns (BIC-1 and BIC-II) conducted from Palestine, Texas, in September 1982 and June 1983. Ozone profiles were obtained which will be compared with similar measurements from other BIC instruments.

Stratospheric Trace Species Measurements with a Balloon-Borne Laser Heterodyne Radiometer

Robert T. Menzies
Jet Propulsion Laboratory

September, 1983

Abstract

The Laser Heterodyne Radiometer (LHR) is an instrument which was designed to measure selected stratospheric trace species by observing their absorption spectra with very high spectral resolution, from stratospheric float altitudes, using the solar occultation technique. The free radical $C\ell O$, which plays a major role in the destruction of ozone by chlorine containing compounds, is the primary species of interest. The balloon-borne LHR, although limited by the solar occultation technique to measurements near local sunset and sunrise, can remotely observe the characteristic infrared spectral features of $C\ell O$ with unique sensitivity and short response times.

Summary of Progress and Results

The LHR has been flown four times since 1978 (being launched from Palestine, Texas on each occasion), and the resulting measurements of $C\ell O$ altitude profiles in the 30-40 km region of the stratosphere have been reported in the journals Applied Optics (vol. 20, pp. 536-544, 1981) and Geophysical Research Letters (vol. 10, pp. 729-732, 1983; vol. 6, pp. 151-154, 1979). The measured profile fits the total column abundance predictions of the latest photochemical models in the 35-40 km region, but the measured profile decreases more rapidly with decreasing altitude than the models indicate, even after accounting for the fact that the measurements were made near local sunset.

The instrument suffered from a faulty photomixer dewar during its last flight, and the replacement dewar also failed during the course of laboratory calibration measurements in 1982. Since that time a new photomixer dewar and optical mounting stage assembly have been designed, fabricated, and tested. The laser local oscillator was also refurbished. The instrument has been reassembled and is ready for a new calibration test. A new set of RF filters has been ordered and will be installed next month. These should improve the spectral discrimination ability of the instrument.

Journal Publications

R. T. Menzies, "A Re-Evaluation of Laser Heterodyne Radiometer $C\ell O$ Measurements", Geophys. Res. Lett., 10, 729-732, 1983.

A: Title: Upper Atmospheric Field Measurements Program: Pressure Modulator Radiometer.

B: Investigator: Dr. Howard K. Roscoe,
168-314 J.P.L.,
4800 Oak Grove Drive,
Pasadena, CA 91109, U.S.A.
and Dept. of Atmospheric Physics,
Clarendon Laboratory,
Parks Road, Oxford OX1 3PU, England.

C: Abstract of Research Objectives:

The Oxford Balloon-borne Pressure Modulator Radiometer, on loan to JPL, measures profiles of stratospheric NO and NO_2 around the day and night. Objectives for 1982 were to participate in NASA-sponsored intercomparison flights together with many other sensors of oxides of nitrogen.

D: Summary of Progress and Results

The Oxford Radiometer flew successfully in both the fall '82 and spring '83 intercomparison flights from Palestine, Texas. In each case it was mounted on a gondola supplied by UK's National Physical Laboratory, and in each case the gondola was damaged due to balloon failure during a first flight attempt.

In fall '82 the radiometer was undamaged after the first attempt, and the successful flight two weeks later gathered NO and NO_2 data for a full day-night for the first time. Data analysis is now almost complete, though the full intercomparison of data will continue during 1984.

The radiometer was damaged during the first launch attempt in spring '83, valves were broken off both detector dewars and the frame was badly dented. However, successful repairs were effected at the launch site, and four weeks later the radiometer worked well during its 12 hour flight. Preliminary data analysis is now complete, though the intercomparison of data has barely started.

A. Title of Research Task:

Far-infrared Measurements of Trace Constituents

B. Investigators and Institutions:

Ira G. Nolt
James V. Radostitz
Department of Physics,
University of Oregon,
Eugene, OR, 97403

C. Abstract of Research Objectives:

Our program objective is to obtain high resolution far-IR emission spectra from balloon platforms in order to establish the simultaneous stratospheric concentrations of certain trace gases critical to tests of ozone photochemistry models.

D. Summary of Progress and Results:

During 1982/1983, we have provided improved detection systems and flight support for two balloon flights of the joint Oregon/Italian far-infrared emission spectrometer in the context of the Balloon Intercomparison Campaign. A three-channel He3-cooled bolometer system, which provides for detector operation at 0.35 kelvin, improved spectrometer performance by an order of magnitude. This detector achieves state-of-the-art performance and is based upon technology pioneered at the University of Oregon. Priority in the two recent balloon flights was given to the following measurements:

1. The ClO mixing ratio from the strength of its rotational emission at $22.9 cm^{-1}$;
2. The NO concentration from its rotational line strength at $32 cm^{-1}$;
3. The HCl and HF concentrations from rotational transitions near $41 cm^{-1}$;
4. Identification of OH emission features.

About forty hours of data near 40 km altitude were recorded in the two flights. Present efforts are concentrating upon the data reduction and analysis. Preliminary analysis indicates the experiment achieved the desired goals.

E. Publication:

"A Three-channel ^{3}He-cooled Bolometer for Sub-mm Balloon Spectroscopy of the Stratosphere," I.G. Nolt, J.V. Radostitz, S. Predko, P.A.R. Ade, J.E. Davis and B. Carli, to be published in Proc. 8th MM Wave Conf., December, 1983.

NEUTRAL SPECIES
IN THE EARTH'S MESOSPHERE AND STRATOSPHERE
A Program for Observation and Instrument Development

Ronald J. Thomas, David W. Rusch, and Ryan W. Sanders
Laboratory for Atmospheric and Space Physics
University of Colorado

ABSTRACT

The objective of this program is to study the photodissociation of ozone near the stratopause. We have measured the ozone density, emission from $O_2(^1\Delta_g)$ and the solar UV penetration. From measurements as a function of altitude both by limb scanning and by a slow descent, we will determine the production rate and quenching of $O_2(^1\Delta_g)$. We will use the data for a calibration check of the Solar Mesosphere Explorer Satellite. The balloon payload consists of a near UV spectrometer for measurement of ozone density and the solar flux from 1900-3200 Å; and a near infrared spectrometer for measuring the $O_2(^1\Delta_g)$ emissions and investigating the surrounding spectral region. All of these instruments were developed for the Solar Mesosphere Explorer Satellite (SME).

PROGRESS AND RESULTS

On April 16, 1983 we had a very successful flight of our balloon payload of two spectrometers (ultraviolet and near infrared), which acquired limb scans under control of a two-axis pointing system which performed excellently. After preliminary analysis, the measurements appear to be very good. An ultraviolet spectrum taken on the limb from a float altitude of

45 km shows the depletion of light near 2500 Å due to ozone absorption. Near infrared data, simultaneously collected, show features of $O_2(^1\Delta_g)$ at 1.27μm and 1.58μm. The ratio of these lines indicates the optical depth of O_2 absorption. The data from these two measurements promise not only to yield information interesting in its own right, but also to provide an excellent calibration check for the Solar Mesosphere Explorer (SME). Ozone data taken by SME on its overflight of the balloon experiment has been reduced. The payload was recovered with only minor damage, and the instruments seem to be in perfect condition.

A. Title of Research Task.

Balloonborne Stratospheric Ultraviolet Imaging Spectrometer.

B. Investigators and Institutions.

Professor Marsha R. Torr
Principal Investigator
Department of Physics
Utah State University
Logan, Utah 84322

Professor D. G. Torr
Co-Investigator
(same institution)

C. Abstract of Research Objectives.

High resolution spectroscopy in the ultraviolet provides the capability to measure several key trace constituents in the middle atmosphere. Examples of such species are OH, ClO, NO, NO_2, and O_3. The radical OH plays an important role in the balance of ozone in the stratosphere. Under this project we have designed an instrument to prove the technique by measuring OH from a stratospheric balloon.

D. Summary of Progress and Results.

During 1982 and 1983 we have completed the design, fabrication and calibration of a high resolution spectrograph. The instrument employs state-of-the-art intensified solid state array detectors and optics. The instrument functions are controlled via computer commands to two on-board microprocessor controllers. The data is telemetered back to the support computer for recording and simultaneous display. The resulting system is entirely the product of a university group and has exposed a number of students at some depth to sophisticated electro-optical, electronic and computing techniques.

In August of 1983 the instrument was successfully flown to the desired altitude of 40km using a helium filled balloon launched by the National Scientific Balloon Facility in Palestine, Texas. The instrument was operated in the stratosphere for several hours and subsequently returned to the ground via parachute and successfully recovered in fully working order for re-use.

The data is now being analysed. Results so far reveal that the project was successful in measuring the OH emissions. The techinque thus represents a powerful method of obtaining previously unavailable data on this important stratospheric constituent.

E. Journal Publications.

In preparation.

A. Stratospheric Temperature and Constituent Distributions from Inversion of Thermal Emission Measurements of the Earth's Limb

B. Mian M. Abbas
Department of Physics and Atmospheric Science
Drexel University
Philadelphia, PA 19104

and

Virgil G. Kunde
Laboratory for Extraterrestrial Physics
Infrared and Radio Astronomy Branch
Code 693
NASA - Goddard Space Flight Center
Greenbelt, MD 20771

C. Abstract

Radiative transfer and inversion programs are being developed for analysis of thermal emission measurements of the earth's stratospheric limb from ballon based platforms. The measurements are planned to be made in the fall of 1983 with a liquid nitrogen cooled Michelson interferometer spectrometer in the spectral range 600-2200 cm^{-1} with spectral resolutions of 0.2 and 0.02 cm^{-1}. The objectives of this research program are to :(i) develop analytical programs for retrieval of temperature and constituent profiles from balloon-based thermal emission measurements (ii) to analyze the observed limb spectra for simulataneous retrieval of temperature and gas constituent profiles. In particular the gases O_3, N_2O, NO_2, NO, CF_2Cl, $CFCl_3$ will be analyzed. (iii) The measurements of variability of the constituent-profiles will be utilized for a comparison with and improvement of stratospheric photochemical models.

D. Summary

During the period sponsored by NASA (April, 1983 to present) radiative transfer and spectral inversion programs are continuing to be developed for retrieval of temperature and gas constituent profiles from limb thermal emission of the earth's stratosphere in the middle infrared. The temperature profile is obtained from an inversion of the observed CO_2 spectrum in the 600 cm^{-1} region with a spectral resolution of 0.2 cm^{-1} . The gas mixing ratio profiles are retrieved from the observed spectral features in the 600-2005 cm^{-1} with a spectral resolution of 0.02 cm^{-1}. The inversion programs employ sharply peaked weighting functions arising from the geometric effects of limb-scanning and the spectral characteristics available with high resolution measurements.

The inversion programs are presently being developed and tested with synthetic thermal emission data for 6 limb-scans with tangent heights at 35, 31, 27, 23 and 19 km. The preliminary results based on synthetic data indicate that with noise-free radiances, temperature profiles with retrieval errors of less than 1K maybe obtained. For synthetic radiances with superimposed noise corresponding to signal to noise ratios of 300-500, the retrieved temperature errors are $\sim$1-1.5k and degrade to 3-5K when the signal to noise ratios are reduced to 60-100. The inversions of gas mixing ratios from syntheitc thermal emission data indicate that retrievals with errors $\sim$10-15% may be retrieved for gases with relatively high mixing ratios such as O_3 and N_2O. The inversions for some additional gases are presently being carried out.

Thermal emission measurements of the earth's stratospheric limb from space platforms require an accurate knowledge of the observation angles for retrieval of temperature and consituent distributions. Without the use of expensive stabilizing systems, however, most observational instruments do not meet the required pointing accuracies, thus leading to large errors in the retrieval of atmospheric data. A self-consistent method has been developed for correcting errors in pointing angles by using information contained in the observed spectrum. The method employs an onion peel iterative algorithm for temperature inversions and the pointing angles for each limb-scan are corrected by using radiances at two appropriately selected frequencies . Numerical results based on temperature inversions of synthetic thermal emission spectra with assumed random errors in pointing angles indicate that errors in observation angles $\sim\pm 0.3$ maybe corrected with temperature retrieval errors <1-2 K

E. Journal Publications:

In preparation

C. GROUND-BASED MEASUREMENTS

TITLE OF RESEARCH TASK: Collecting, Analyzing and Archiving of Infrared Solar Spectra from Denver and Mt. Evans

INVESTIGATORS: David G. Murcray, Physics Department, University of Denver
Aaron Goldman, Physics Department, University of Denver
Frank J. Murcray, Physics Department, University of Denver

RESEARCH OBJECTIVES:

The infrared solar spectrum as observed from the ground under high resolution contains thousands of absorption lines. The majority of these lines are due to compounds that are present in the Earth's atmosphere. Ground based infrared solar spectra therefore contain information concerning the composition of the atmosphere at the time the spectra were obtained. The objective of this program is to obtain solar spectra from various ground locations, and to analyze and archive these spectra. The analysis consists of determining, for as many of the absorption lines as possible, the molecular species responsible for the absorption. Archiving is an important part of the program since a number of the features in the spectra have not been identified. At some later time, when the features are identified, it will be possible to determine the amount of that compound that was present in the atmosphere at the time the spectrum was taken.

SUMMARY OF PROGRESS AND RESULTS:

Since ground based solar spectra can be taken daily (weather permitting), they offer a technique for studying the short term variability of constituents which can be measured by this technique. The question of the short term variability of the constituents being measured during the Balloon Intercomparison Campaign (BIC) was of considerable concern (particularly if the balloon launches were separated in time). In view of this, provision was made to operate our solar interferometer system from the ground at Alamogordo NM during the periods the balloon flights of the intercomparison were scheduled to be flown. The weather at Alamogordo was particularly bad during the period covering the BIC I campaign (late September, 1982) and no useful data were obtained. The BIC II campaign extended over a much longer time frame. For the second BIC the unit was operated at Alamogordo starting April 23, 1983. Data were taken at either sunrise or sunset (or both) on April 23, 24, 26, 30, May 1 through 9, and May 16. Data were taken again on June 17 through 20. The second series covers the dates of the flights (June 17 and 20). For these measurements the instrument was set to scan the 2800 cm^{-1} to 3000 cm^{-1} region where the $HC\ell$ lines occur and the 750 cm^{-1} to 1200 cm^{-1} region which covers several HNO_3 bands.

Collecting, Analyzing and Archiving of Infrared
Solar Spectra from Denver and Mt. Evans

Ground based solar spectra are usually used only to determine total column amounts of a compound. The technique would be more valuable if some altitude profile information could be retrieved from the spectra. As the resolution achieved in these studies has increased, it has become possible to use the shape of the absorption lines to obtain information on the altitude distribution of the constituent. As part of the work performed on this grant we have done a study on ground based solar spectra to determine the extent of the altitude information available in such spectra. These results are encouraging and are contained in the publication listed below. The study is being continued on higher resolution spectra.

JOURNAL PUBLICATION:

Goldman, A., F. G. Fernald, F. J. Murcray, F. H. Murcray and D. G. Murcray, "Spectral Least Squares Quantification of Several Atmospheric Gases from High Resolution Infrared Solar Spectra Obtained at the South Pole," J. Quant. Spectrosc. Radiat. Transfer, 29, 189-204, 1983.

TITLE: Experimental Studies of Atmospheric N_2O, NO, CH_3Cl and CH_3Br

INVESTIGATORS: Michael B. McElroy and Steven C. Wofsy

INSTITUTION: Harvard University, Cambridge, Massachusetts 02138

PROGRAM SUMMARY

Experimental studies are focussed on sources and sinks for important trace gases of the atmosphere, including N_2O, CH_4, CH_3Cl and CH_3Br. We are examining production and consumption of these gases by bacteria, fungi, soils and aquatic systems and are investigating production of selected species by combustion of coal, oil and wood fuels and by several additional industrial processes. Our work involves measurements both in the field and the laboratory. It is motivated by a goal to elucidate processes which affect the abundance of important atmospheric gases on a global scale.

PROGRESS REPORT

We carried out experimental studies of sources and sinks for atmospheric trace gases, including N_2O, CH_4 and light alkanes. Field trips to South America showed that soils in tropical moist forests are important sources for atmospheric N_2O, but these soils consume atmospheric methane. Careful measurements of atmospheric composition revealed excesses of both N_2O and CH_4 over the interior of the continent. It is likely that seasonally flooded wetlands of the great rivers provide major inputs of CH_4. Data on distributions of N_2O and CH_4 over Brazil have been analyzed using the Harvard/GISS GCM tracer model. The model reproduces many features of the observed concentration gradients. The results indicate that tropical South America provides 25-50% of the global source of N_2O.

Studies of combustion of No. 6 fuel oil and of coal show that N_2O is produced promptly during the first stages of combustion. Both N_2O and NO emissions appear to depend on fuel N content and on redox conditions during the first stage of combustion.

The interaction of the Amazon River with the waters of the Atlantic Ocean were studied in a series of three oceanographic field programs. The results show that bound phosphorus is mobilized from suspended sediment as it is reworked by tidal currents along the northeastern coast of Brazil. There does not appear to be an analogous process for nitrogen, which is more directly under biological control.

PUBLICATIONS

Hashimoto, L.K., W.A. Kaplan, S.C. Wofsy, and M.B. McElroy (1983). Transformations of fixed nitrogen and N_2O in the Cariaco Trench. Deep Sea Res. 30, 575-590.

Fox, L.E. and S.C. Wofsy (1983) Kinetics of removal of iron colloids from estuaries. Geochimica Cosmochimica Acta 47, 211-216.

McElroy, M.B. (1982) Marine biology: controls on atmospheric CO_2 and climate. Nature 302, 328-330.

Measurement of Concentration and Variation in Stratospheric Chlorine Monoxide from a Portable Gound Based Millimeter Wave System

P. M. Solomon and R. L. de Zafra
Co-Principal Investigators
State University of New York, Stony Brook, N.Y.

Abstract of Research Objectives

The purpose of this research is to measure stratospheric CℓO and related trace species involved in stratospheric ozone chemistry and possible ozone depletion, such as HO_2, H_2O_2, HOCℓ, NO, etc. Measurement of temporal and latitudinal variations is an important goal, as well as measurement of average values. The technique employs a uniquely designed ground-based mm-wave heterodyne receiver for the measurement of rotational emission line spectra from the trace gases of interest. Stratospheric column densities and approximate vertical distributions are determined from absolute line intensity and pressure-broadened line shape measurements. A number of sites with good global latitude coverage are available, three such sites have been used to date, one Mauna Kea, Hawaii providing year-round useability and exceptionally high quality data.

Summary of Progress and Results (1982-83)

During 1982 and 1983 chlorine monoxide was measured from sites in Massachusetts, Arizona and Hawaii. The average daytime quantity of CℓO above 30 Km was found to be close to that expected from current chemical models of the stratosphere which assume about 2.2 parts per billion of total chlorine. We also succeeded in measuring the chlorine monoxide content above 30 kilometers around the clock showing a decline from mid-day to early morning with a day/night ratio of 8:1 providing a critical test of the chlorine chemistry.

These ground-based results establish

1) The presence of chlorine monoxide in concentrations close to that predicted by use of measured reaction rates
2) The existence of a nighttime reservoir of chlorine, most likely $C\ell ONO_2$
3) The predicted rate of storage and retrieval from this reservoir is in fairly good agreement with the data, and
4) The basic chemistry of chlorine and its compounds above 30 Km is reasonably well understood.

We have also detected and measured signals from the stratospheric radical HO_2, an important rate-limiting trace species involved in the stratospheric ozone cycle. To the best of our knowledge, these are the first observations of this trace-gas to be made since some early detections in 1976 and 1977. Our current data gives indirect evidence of a discrepancy with these earlier measurements, but different and only slightly overlapping altitude ranges are covered, and HO_2 may show large temporal fluctuations due to variability of the parent water-vapor reservoir. More observations are planned.

We have conducted a brief series of observations on stratospheric N_2O and have achieved a new upper limit on the column density of H_2O_2 above ~30 Km. The latter data is undergoing final analysis, but seems to indicate an upper bound at least as low as the value generated by current chemical modelling. Further observations are planned during the coming year.

Publications

1) A Measurement of Stratospheric HO_2 by Ground-Based mm-Wave Spectroscopy; R. L. de Zafra, A. Parrish, P. M. Solomon, and J. W. Barrett (to be published in J. Geophys. Res.)

2) Observation of Diurnal Variation of Stratospheric $C\ell O$: A Critical Test of Chlorine Chemistry in the Ozone Layer; P. M. Solomon, R. L. de Zafra, A. Parrish, and J. W. Barrett (submitted to Science, Aug. 1983).

3) A Quasi-Continuous Record of Atmospheric Opacity at $\lambda = 1.1$ mm over 34 Days at Mauna Kea Observatory; R. L. de Zafra, A. Parrish, R. M. Solomon, and J. W. Barrett; To be published in Int. J. IR and mm Waves, Sept. 1983.

Summary Report for the Grant
"Studies of Upper-Atmosphere Motions by VHF Backscatter"
NSG 7506

A. Title: Studies of Upper-Atmosphere Motions by VHF Backscatter

B. Investigator and Institution: S. A. Bowhill
Department of Electrical Engineering
University of Illinois
Urbana, IL 61801

C. Research Objectives:

The purpose of this research is to use the Urbana coherent-scatter radar to observe the upper troposphere, lower stratosphere and mesosphere, and to interpret these results in terms of dynamical processes in these regions of the atmosphere.

D. Summary of Progress and Results:

The intensity of turbulence and its line-of-sight velocity has been measured on a campaign basis through 1982 at Urbana, Illinois, and on a daily basis commencing in March 1983. These results are analyzed to give the intensity and spectrum of stratospheric gravity waves, and the southeasterly component of the hourly average horizontal velocity from 9 to 24 km altitude. Extensive comparisons of these winds with those measured from a nearby radiosonde station showed good agreement; this agreement is generally better in the lower stratosphere where the winds show less horizontal variability over the distance separating the radar from the radiosonde station.

The Urbana location is unique for this type of radar in that it is located in flat terrain where orographic force of gravity waves is negligible. Radar observations in the vicinity of thunderstorms indicate that gravity-wave amplitudes increase by a factor of 3 or more during periods of intense nearby convective activity. In addition, it has been possible to identify strong vertical motions around 10 km in the clear air above thunderstorm activity.

The intensity of scatter from the turbulence at levels throughout the altitude region studied has been shown to be correlated with the hydrostatic stability of the region. Power spectra of the measured line-of-sight velocities change with altitude, and have been shown to correlate with corresponding changes of the Brunt Viasala frequency. In the lower stratosphere, these spectra are often found to be nearly monochromatic for periods of at least two hours, indicating that some form of filtering is occurring from the origin of excitation for frontal or convective activity.

Studies of these waves are continuing to determine their role in enhancing turbulent mixing in the stratosphere over local regions of severe weather disturbances.

E. Publications

An investigation of turbulent scatter from the mesosphere as observed by coherent-scatter radar, by K. P. Gibbs and S. A. Bowhill, Aeronomy Report No. 110, Aeron. Lab., Dep. Elec. Engr., Univ. Ill, Urbana-Champaign.

Observations of the upper troposphere and lower stratosphere using the Urbana coherent-scatter radar, by L. D. Goss and S. A. Bowhill, Aeronomy Report No. 111, Aeron. Lab., Dep. Elec. Engr., Univ. Ill, Urbana-Champaign.

VHF power scattered from the mesosphere at midlatitudes, by O. Royrvik, K. P. Gibbs, and S. A. Bowhill, J. Geophys. Res., 87, 2501-2508, 1982.

Faster compilation by multithread hashing, by S. A. Bowhill, 1982 FORML Conference Proceedings, 25-38, 1983, FORTH Modification Laboratory, Palo Alto, CA 94070.

Fast local variables, by S. A. Bowhill, 1982 FORML Conference Proceedings, 142-146, 1983, FORTH Modification Laboratory, Palo Alto, CA 94070.

ALPHAKEY file management system, by S. A. Bowhill, 1982 FORML Conference Proceedings, 239-250, 1983, FORTH Modification Laboratory, Palo Alto, CA 94070.

Mesospheric scatter and its microstructure, by S. A. Bowhill and K. P. Gibbs, Handbook for MAP, Vol. 9, in the press.

Pulse stuttering as a remedy for aliased ground backscatter, by S. A. Bowhill, Handbook for MAP, Vol. 9, in the press.

Nighttime mesospheric returns associated with a large solar flare event, by S. A. Bowhill, Handbook for MAP, Vol. 9, in the press.

A comment on some drawbacks of monostatic radar, by S. A. Bowhill, Handbook for MAP, Vol. 9, in the press.

Spaced antenna drift, by O. Royrvik, Handbook for MAP, Vol. 9, in the press.

Implication of data interpretation by short- and long-period oscillations, by O. Royrvik, Handbook for MAP, Vol. 9, in the press.

Effects of geophysical noise on the accuracy of wind determination, by S. A. Bowhill, Handbook for MAP, Vol. 9, in the press.

The Urbana MST radar, capabilities and limitations, by O. Royrvik and L. D. Goss, Handbook for MAP, Vol. 9, in the press.

Design considerations for MST radar antennas, by S. A. Bowhill, Handbook for MAP, Vol. 9, in the press.

Real-time MST-radar signal processing using a microcomputer running under FORTH, by S. A. Bowhill, Handbook for MAP, Vol. 9, in the press.

Review of correlation techniques, by S. A. Bowhill, Handbook for MAP, Vol. 9, in the press.

A. Title of Research Task - "Stratospheric Dynamics - Observational Studies."

B. Investigators and Institutions -

D. T. Farley and M. F. Larsen (Cornell University)
R. F. Woodman, consultant, (Geophysical Institute, Lima, Peru)
M. Ierkic (Arecibo Observatory)

C. Abstract of Research Objectives -

Although stratospheric turbulence is characterized by scale sizes of only hundreds of meters in the vertical and tens of kilometers in the horizontal, these turbulent processes are important even for large-scale transport and the total energy budget. We still know very little about the morphology and dynamics of turbulence in the lower stratosphere primarily due to the difficulties in making measurements at small temporal and spatial scales above the boundary layer. The Arecibo Observatory 430 MHz radar is capable of measuring winds and turbulence characteristics between 6- and 25-km altitude with a time resolution of approximately 1 min and a height resolution of 150 m. The radar is capable of detecting the small amount of incident energy that is backscattered by variations in the refractive index. Over 300 hours of data have been gathered and this unique data set is being used to study turbulence, its sources and effects. At the same time, old equipment is being reconfigured to provide data with 30 m height resolution, so that the individual structures can be resolved.

D. Summary of Progress and Results -

Prior to 1982 the work focused primarily on obtaining a suitable data base for studying stratospheric turbulence and on developing the software required for routine processing of the large amounts of data. Recently, the effort has focused on analysis of the available data along with a parallel effort to observe the turbulent structure with improved height resolution. The radar reflectivity data have shown that stratospheric turbulence occurs in layers, in agreement with earlier results, and the large data base has given good estimates of the frequency of occurrence of the layers and the layer thickness distribution. Rastogi and Woodman (1983) have used the observed characteristics to model the transport (diffusion) of a tracer by the sweeping, intermittent layers. They have calculated a value for the diffusion coefficient of 0.1-0.3 m^2/s, an order of magnitude larger than the values derived from aircraft measurements made in the early 1970's. The modeling has also shown that though the layers are discrete, diffusive-type mixing still takes place even when there are only relatively few realizations of layer mixing within the height range studied.

Nearly all of the theories of turbulence for both isotropic and stratified media relate to the dynamics of the k (wavenumber) spectrum. Although the layer description provides an adequate description of the diffusive process, it is not immediately evident how this process is related to the theoretical developments. We are presently investigating the wavenumber spectra based on their location in relation to the turbulent layers. It appears that the spectra within the more turbulent regions are more flat than those in less turbulent regions. The steeper spectra are more characteristic of an inertial subrange, whereas the flatter spectra may be an indication of a source of turbulence. Preliminary results show better agreement with Weinstock's (1978) theoretical treatment of stratified turbulence than with other treatments.

Finally, the vertical wavenumber spectra are being used to investigate whether mesoscale turbulence is characterized by two- or three-dimensional processes. There are important implications about the direction of flow of energy along the wavenumber spectrum depending on which process dominates (see the summary by Larsen, 1983). If the turbulence is two-dimensional, energy will flow from small to large scales. The flow direction will be reversed in three-dimensional turbulence. In either case, the problem is of importance for mesoscale modeling.

E. Journal Publications -

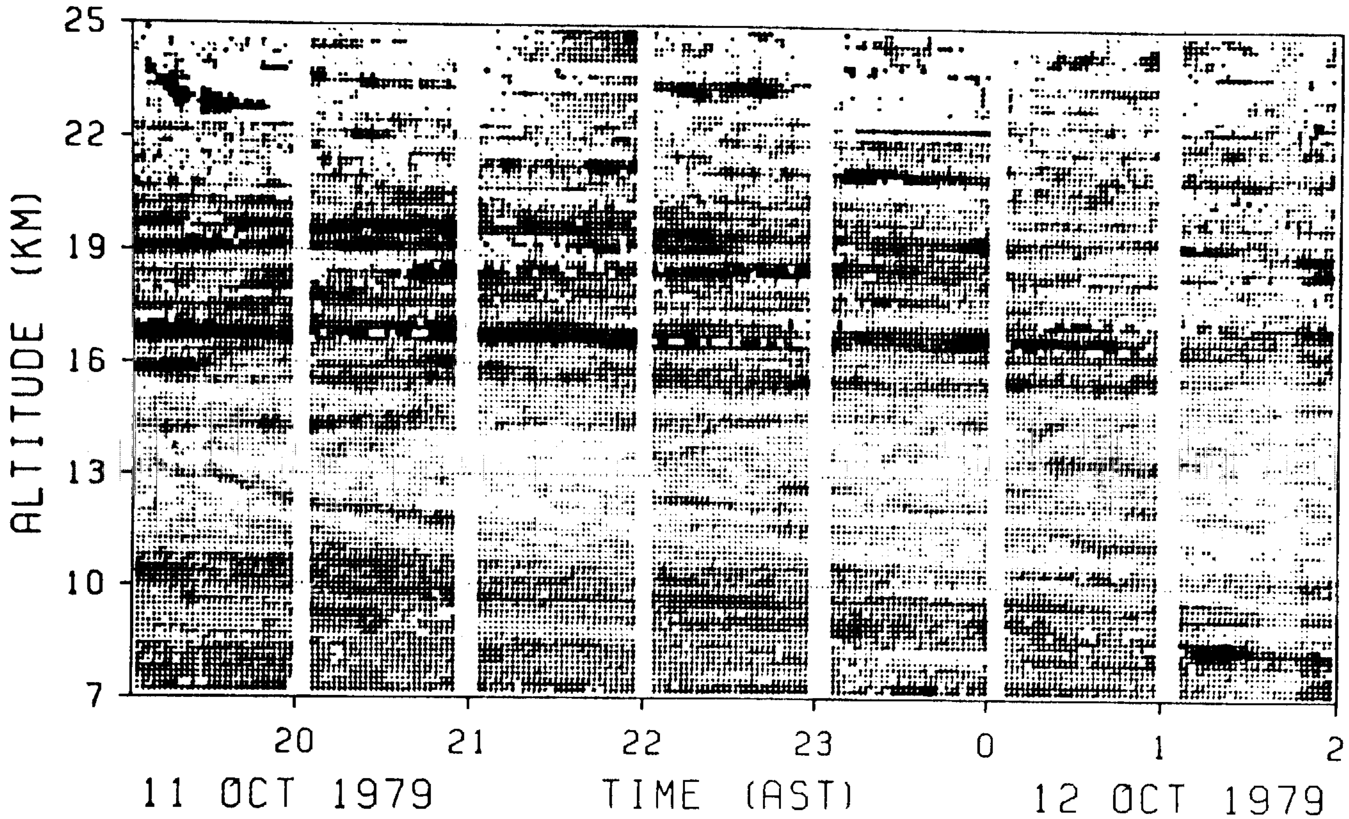
Fukao, S., T. Sato, N. Yamasaki, R. M. Harper, and S. Kato, Winds measured by a UHF Doppler radar and rawinsondes: Comparisons made on twenty-six days (August-September 1977) at Arecibo, Puerto Rico, J. Applied Meteorol., 21, 1357, 1982.

Larsen, M. F., The MST radar technique: A tool for investigations of turbulence spectra, Invited review, Workshop on MST Radar Technique, To be published in the MAP Handbook Series, University of Illinois, Urbana, Illinois, 1983.

Rastogi, P. K., and R. F. Woodman, Vertical transport in the tropo-stratosphere by intermittent turbulence: A simulation study, Preprint Volume, Sixth Symposium on Turbulence and Diffusion, March 22-25, 1983, Boston, Mass., American Meteorological Society, Boston, Mass., 256-268, 1983.

Sato, T., and R. F. Woodman, Fine altitude resolution observations of stratospheric turbulent layers by the Arecibo 430 MHz radar, J. Atmos. Sci., 39, 2546, 1982.

Sato, T., and R. F. Woodman, Fine altitude resolution radar observations of upper-tropospheric and lower-stratospheric winds and waves, J. Atmos. Sci., 39, 2539, 1982.



8-level height–time shade plot of the echo power. The dynamic range is 32 dB. Missing points due to poor quality of data left blank.

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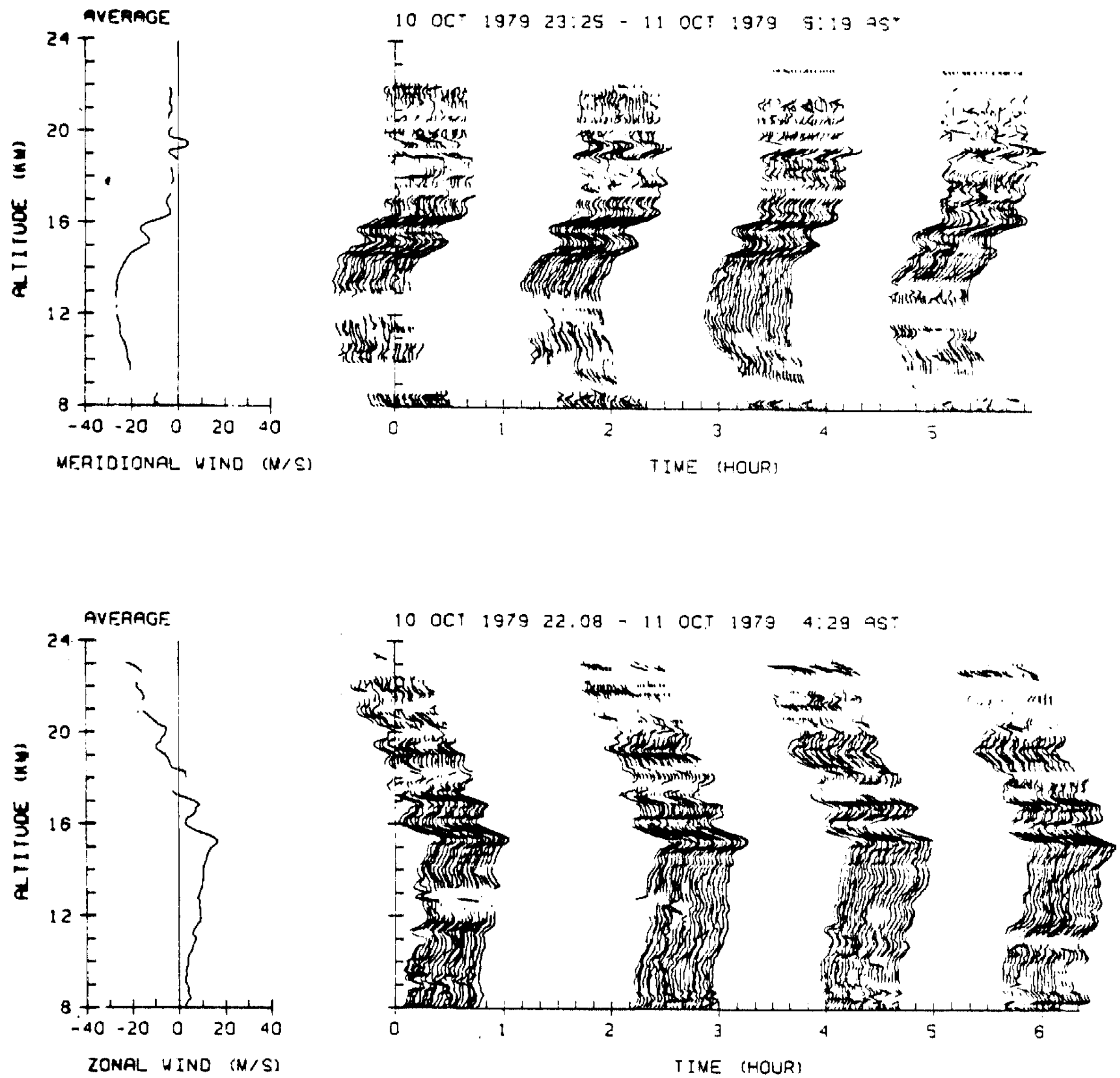

. Zonal and meridional wind velocity versus height and time. Height profiles are plotted side-by-side, spaced according to the observed time. The time scale is measured from the beginning of observed time. Zero hours correspond to the times indicated above the profiles.

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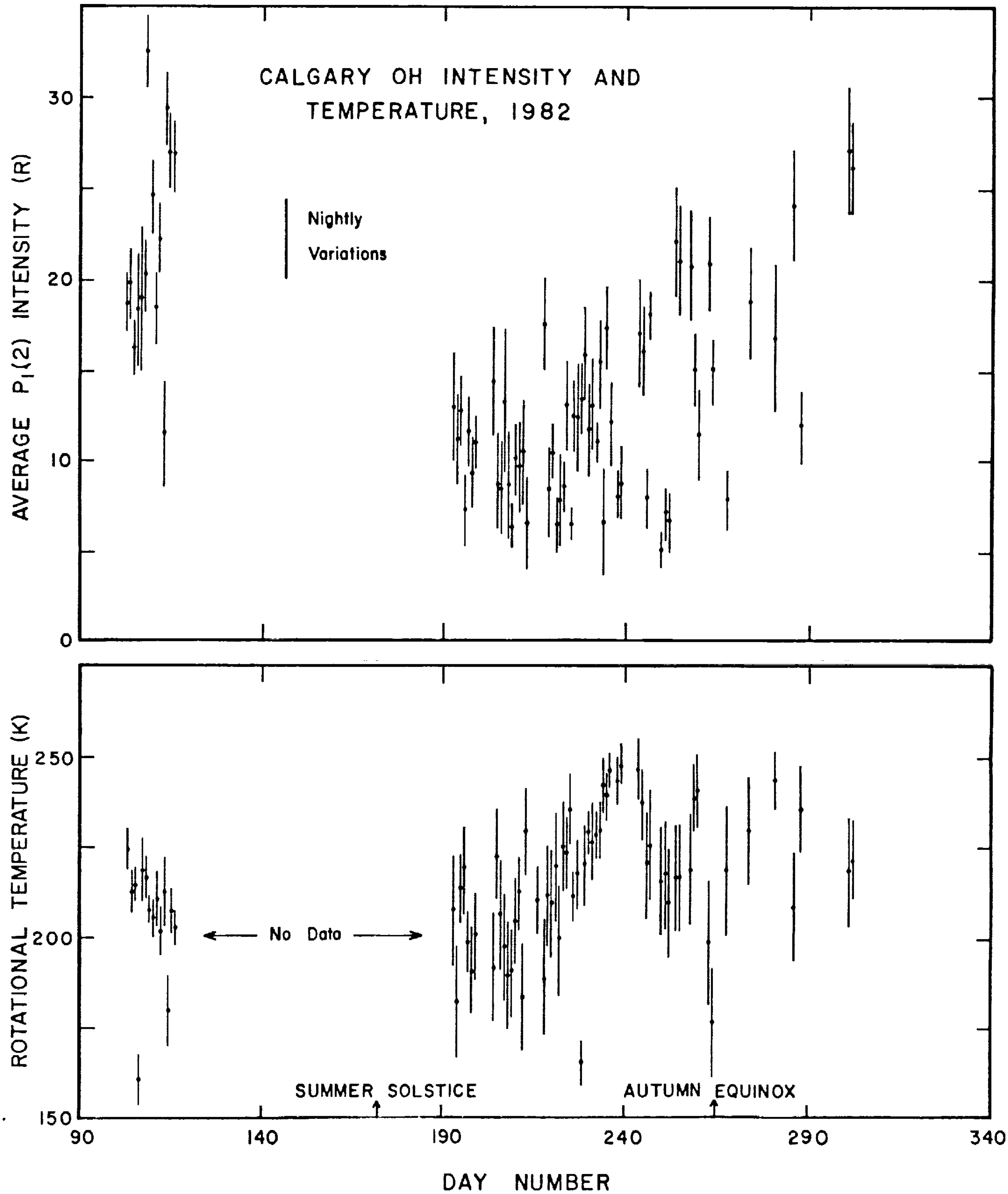
Summary report of activities: Thermal mapping of the mesosphere

We have carried out observations on the mesospheric temperature at a location near Calgary, Alberta, near the Canadian Rockies. The method used involves the relative intensity measurement of two rotational lines of a molecular band of OH, from which the rotational temperature can be inferred. This work has been conducted using a tilting filter photometer scanning along the meridian between elevation angles of 20 degrees in the north and south of the station. These observations are monitored by means of telecommunication link to the site from our laboratory. Preliminary examination of 6 months of the observations shows an annual variation of about 35 degrees with warmer values found during the winter months. These results are shown in Figure 1.

We have also installed at this site a 1 m spectrometer to carry out simultaneous observations of mesospheric airglow emissions such as sodium and Herzberg band emissions. It is expected that these emissions will show correlations with the OH emissions during times of stratospheric warmings. This instrument was borrowed from Dr. Charles Barth, University of Colorado.

Our plans for the oncoming year includes a more intensive search for thermal variations related to gravity wave structure in the mesosphere. As a part of this work, we intend to set up an automatic instrument using the same technique outlined above that would observe mesospheric temperatures in conjuction with a MST radar operated by Dr. Gene Adams at Boulder, Colorado. There will also be made at the same site TV imaging observations of the OH surface brightness. It will be possible to direct the tilting filter photometer to observe the temperature distribution in real time in a line of positions across a wave feature observed with the imaging system. The radar will characterize the mesospheric wind system.

Finally, we have written for the MAP handbook edited by Dr. Robert Vincent a review paper entitled "Ground-based measurements of the mesospheric temperature by optical means".


CALGARY OH INTENSITY AND TEMPERATURE, 1982
AVERAGE $P_1(2)$ INTENSITY (R)
Nightly Variations
0
10
20
30
ROTATIONAL TEMPERATURE (K)
150
200
250
No Data
SUMMER SOLSTICE
AUTUMN EQUINOX
90
140
190
240
290
340
DAY NUMBER

FLUOROCARBONS, CHLOROCARBONS AND NITROUS OXIDE: CONTINUOUS MEASUREMENTS AT 5 GLOBAL SITES

Richard D. Rosen, Ph.D.
Principal Investigator

Atmospheric and Environmental Research, Inc. (AER)
840 Memorial Drive
Cambridge, Massachusetts 02139

August 1983

Abstract of Research Objectives

Measurements of the halocarbons $CFCl_3$, CF_2Cl_2, CCl_4 and CH_3CCl_3 and also of nitrous oxide are being made about four times daily at each of five sites around the globe. Comparison of the measurements for the halocarbons with estimates of their emission rates enables calculations of their global circulation rates and globally-averaged atmospheric lifetimes. This Atmospheric Lifetime Experiment is a multidisciplinary research program in which our role at AER has been to process the station data and to contribute to their analysis.

Summary of Progress and Results

The Atmospheric Lifetime Experiment began in July 1978 under the sponsorship of the Chemical Manufacturers Association. In July 1982, our efforts at AER became supported by NASA's Upper Atmospheric Research Program. Under this support, a fourth year of station data has been placed into final form and a fifth year of station data has undergone initial processing and error checking.

Results based on the first three years of data from the Experiment are being reported in a series of articles being published in the scientific literature. The newer data collected since NASA's involvement in the Experiment represent an important extension of the data base. A preliminary analysis of the new data indicates that the error levels in our estimates of the species' trends are significantly reduced by these data's addition to the time series.

Statistical analysis tools have been developed at AER to quantify the interrelationships among the different species at the different stations. Preliminary results based on the first three years of data were encouraging, and this analysis will, therefore, be pursued with the additional data now available.

Journal Publications

No papers were published during 1982-83 that contained results generated with funds provided to AER by NASA.

1982-83 FY SUMMARY

A. Title of Research Task: Long-Term Ambient Monitoring of N_2O and the Halocarbons

B. Investigator and Institution: Dr. Dagmar R. Cronn, Principal Investigator
Prof. Elmer Robinson
Laboratory for Atmospheric Research
College of Engineering
Washington State University
Pullman, Washington 99164-2730

C. Abstract of Research Objectives: Almost continuous measurements have been made of four halocarbons (F-12, CCl_2F_2; F-11, CCl_3F; methyl chloroform, CH_3CCl_3; and carbon tetrachloride, CCl_4) and nitrous oxide, N_2O, at a rural site near Pullman, Washington (47°N) since mid-1976. The purpose of this measurement program has been to document the changes in the atmospheric levels of these five trace gases on both an annual and a seasonal basis. Increases in these gases are important because they can deplete the natural concentration of ozone in the stratosphere. Existence of increased levels of these gases in the atmosphere also can lead to global warming of the earth through the greenhouse effect. A secondary objective of this research has been to relate small short-term changes (on the order of a few days) to synoptic meteorology. Understanding this relationship has provided information about the mechanisms which transport and mix these gases globally.

D. Summary of Progress and Results: Table 1 shows the rates of increase for each of the five trace gases based on a linear regression fit to the weekly averaged mixing ratios. The data set prior to June, 1981 has been obtained by digitizing peak heights. This task of digitizing the older data has been accomplished in the last two years to improve the precision of the data. Data reported subsequent to June, 1981 have been acquired using a new automatic data acquisition system which provides adequate precision without the need for manual data reduction. Table 1 indicates the mixing ratios of each compound both at the beginning of the reporting periods for each compound and in May, 1983.

TABLE 1

	Rate of Increase		Beginning Mixing Ratio (Date)	Ending Mixing Rate (5/13/83)
N_2O	0.94±0.15 ppb/yr	0.30±0.05%/yr	297 ppb (6/12/76)	303.5
F-12	12.15±0.39 ppt/yr	4.4±0.14%/yr	276 ppt (3/4/78)	339
F-11	6.87±0.25 ppt/yr	4.2±0.15%/yr	164 ppt (12/17/77)	201
CH_3CCl_3	9.38±0.38 ppt/yr	7.8±0.32%/yr	120 ppt (12/17/77)	171
CCl_4	3.42±0.34 ppt/yr	2.4±0.24%/yr	141 ppt (12/17/77)	166

The 0.3% per year estimate of the N_2O rate of increase for the seven-year period from mid-1976 to mid-1983 is in good agreement with the rate of increase of 0.2% year reported by R. F. Weiss (J. Geophys. Res., 86, 7185-95, 1981). The rates of increase given in Table 1 for the trace gases are preliminary estimates which may change slightly when the final data quality check is completed and data back to 1976 added for the remaining four trace gases to the approximately 150,000-line data set.

The atmospheric mixing ratios of F-12 and F-11 increase abruptly up to 14 ppt for F-12 and 8 ppt for F-11 after strong cold fronts pass across the sampling site. This means air masses from higher latitudes (>60°N) can have F-12 and/or F-11 mixing ratios as much as 5% higher than mid-latitude air masses. An explanation for the results is that anthropogenic, chemically stable compounds such as F-12 and F-11 are emitted into mid-latitude air masses which move preferentially northward to the polar regions, similar to the trajectories proposed for arctic haze precursors. These compounds become incorporated into polar air masses and are subsequently returned to mid-latitude regions via synoptic scale air mass motions. As the air masses lose their identity during the frontolysis process the halocarbons and other stable trace constituents are diluted into the mixing, southern, air masses and become part of the gradually increasing global background for these compounds. Nitrous oxide, as a non-anthropogenic, relatively stable, and much more uniformly emitted compound does not have a consistent air mass differential and does not follow the pattern mentioned above for halocarbons. A similar analysis has not been made for CH_3CCl_3 and CCl_4.

E. Journal Publications:

Cronn, Dagmar, Elmer Robinson, W. Lee Bamesberger, and Michael Carter, Long-term monitoring of nitrous oxide and halocarbons, paper 3A.7 in proceedings of the Second Symposium on the Composition of the Nonurban Troposphere, Williamsburg, VA, May 25-28, 1982, pp. 64-67. Published by the American Meteorological Society, Boston, MA.

Carter, Michael W., Halocarbon Concentration Patterns Associated with Frontal Passages, Masters thesis, Washington State University, Pullman, WA, June, 1983.

Cronn, Dagmar R., W. Lee Bamesberger, and Valentin M. Koropalov, Abastumani forest aerosol experiment (1979): Comparison to other nonurban halocarbons and nitrous oxide measurements, Environmental Science and Technology, 17, 383-388, 1983.

Nutmagul, Winai and Dagmar R. Cronn, Distribution of atmospheric methyl chloride, submitted to Journal of Geophysical Research, 1983.

SUMMARY FOR NASA RESEARCH GRANT 836-UA-272/AQ-94

A. "Latitudinal Gradients in Tropospheric Concentrations of Selected Halocarbons and Hydrocarbons"

CONTRACT STARTING DATE: March 15, 1983

B. Principal Investigator: Prof. F. Sherwood Rowland

Institution: Department of Chemistry
University of California
Irvine, California 92717

C. Research Objectives: Measurements of the tropospheric concentrations of methane and four chlorocarbon compounds (CCl_3F, CCl_2F_2, CCl_4, CH_3CCl_3) are made four times each year at approximately 25 locations covering the latitude range from 71°N to 50°S. These data provide an accurate estimate of the distribution of these gases on a fine latitude grid once each season, as well as an inventory for each of the total worldwide atmospheric concentrations each season. The inventories for CCl_3F and CCl_2F_2 provide regular estimates of the continuing emissions of these gases into the atmosphere, and have been used as empirical inert tropospheric tracers to monitor the transport of trace chemical species from north to south. The inventory and latitudinal distribution for CCl_4 have indicated so far complete consistency with the hypothesis that all of this compound is of man-made origin. Further measurements will provide data on the current yearly emissions. The concentrations and distribution of CH_3CCl_3 are affected by emissions, latitudinal transport and also by the tropospheric reaction rates with hydroxyl (OH) radicals, the major process by which it is removed from the atmosphere. The measurements of tropospheric methane provide the data needed to determine whether it is continuing to increase in concentration at all latitudes as indicated by our data since 1978. These data also provide information about seasonal emissions and losses of methane, and must be consistent with the same hydroxyl distribution applicable to the data for CH_3CCl_3.

D. Summary of Progress and Results for the period Mar.15–Aug.15, 1983

One latitudinal distribution has been measured for methane and each of the halocarbons for a collection period around April 15, 1983. The sites for this series included Alaskan sites from Barrow to Ketchikan, west coast of the U.S. and Baja California, numerous Pacific Islands from 21°N to 29°S and from New Zealand to 47°S. The methane concentrations in the northern hemisphere were about 1.71 ppmv in Alaska and about 1.69 in the north temperate zone. The concentrations from 8°S to 47°S were all within 1.56 ± 0.01, indicating very thorough mixing through most of the southern hemisphere. The methane concentrations decrease smoothly across the central tropical latitudes from 20ON to 8°S, indicating a sharp separation into the two hemispheres. The ratio in methane concentrations between the northern and southern hemispheres in April was higher than measured previously in other seasons, while showing continued increase in the worldwide methane inventory. The distributions for all four chlorocarbons (CCl_3F, CCl_2F_2, CCl_4, CH_3CCl_3) also showed smooth breaks in concentrations from 20°N decreasing to 8°S, together with nearly constant concentrations from 8°S to 47°S.

The empirical transport model based on the latitudinal distribution for CCl_3F fits quite satisfactorily for both CCl_2F_2 and CCl_4. The best fit to the north/south distribution for CH_3CCl_3 is obtained with approximately equal removal by reaction with OH radicals in both hemispheres. The methane distribution versus latitude is consistent with a calculated 80% release in the northern hemisphere, together with the OH distribution utilized for CH_3CCl_3. Preliminary calculations and measurements with shorter-lived halocarbons such as $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$ show general consistency with the transport and hydroxyl radical reaction parameters deduced from the other halocarbon measurements. Comparison of the present methane data with measurements made in the past shows the need for seasonal dependence in both the hydroxyl reaction rates, and probably in the transport parameters as well. Tests of such seasonal dependences are under way using the distributions of the shorter-lived halocarbons.

The second set of atmospheric collections is being made during August and the results of the measurements should be available by late September.

E. Journal Publications: None. One abstract each has been accepted on methane and on halocarbons for the WMO meeting in Vienna, Austria, October 17-21, 1983, with full papers due in January, 1984.

A. Ground-Based Observations in Support of 1983 Balloon Intercomparison Campaign

B. Gerald M. Stokes and Douglas W. Johnson
Battelle Pacific Northwest Laboratories

C. The research objectives of this task are to provide ground-based observations of several important stratospheric trace species in conjunction with the Spring 1983 Balloon Intercomparison Campaign based in Palestine, TX. The species observed were HF, HCl and HNO3 using the 1-meter Fourier Transform Spectrometer at Kitt Peak National Observatory in absorption against the sun.

D. The results to date consist of equivalent widths measured for the absorption features listed.

HCl - P5, P3 and R1
HF - R1

These measurements are then incorporated into an atmospheric model in which an assumed vertical distribution is used to calculate the effective airmass as a function of solar zenith angle. In addition the temperature structure is taken from rawinsonde data taken at the Tucson International Airport, approximately 60 km distant.

The result of these calculations is the ratio of an assumed distribution to that which would produce the observed absorption. In essence it is a scaling factor for the assumed distribution. We are continuing work related to extraction of vertical profile information from the observations. The two main approaches are to use the temperature sensitivities of the HCl lines to estimate the effective line temperatures and to consider the detailed line growth at larger solar zenith angles.

Both of these items, particularly the large zenith angle data, indicate that vertical distribution information remains in the data after assuming a constant mixing ratio above 15 km for HCl, and constant above 20 km for HF.

SUMMARY OF UPPER ATMOSPHERIC RESEARCH

A. Title of Research Task

"Ground-based Measurements of Stratospheric $C\ell O$"

B. Investigators and Institutions:

Dr. Michael J. Mumma
Dr. Drake Deming
Dr. Theodor Kostiuk
Dr. John J. Hillman

All at:

Infrared and Radio Astronomy Branch
Code 693
NASA/Goddard Space Flight Center
Greenbelt, MD 20771

C. Abstract of Research Objectives

Doppler limited infrared spectroscopy is used to investigate stratospheric molecules. The technique is to observe terrestrial spectral lines formed against the solar continuum in the 9-12μm wavelength range. An infrared heterodyne spectrometer is used to achieve spectral resolutions ($\lambda/\Delta\lambda$) approaching 10^7, and a ratio of signal-to-noise on the solar continuum approaching 30,000. This permits the determination of column abundances of trace constituents in the stratosphere, and also their altitude distribution in favorable cases. Supporting laboratory spectroscopy and theoretical studies are carried out.

D. Summary of Progress and Results

Chlorine monoxide ($C\ell O$) is thought to play an important role in a photochemical cycle which causes the destruction of ozone in the earth's stratosphere. Since lines of the (1,0) fundamental of $C\ell O$ lie near $^{14}C^{16}O_2$ laser lines, IR heterodyne spectroscopy is potentially an important technique for monitoring the $C\ell O$ abundance. However, lines from other trace atmospheric gases also exist in this spectral range, and the interpretation of such observations could be ambiguous unless high-resolution laboratory measurements supported the identifications. We have measured frequencies for spectral lines of seven trace atmospheric gases which absorb near the $^{14}C^{16}O_2$ laser transitions relevant to the detection of $C\ell O$ by IR heterodyne spectroscopy. The gases measured were OCS, NO_2, HNO_3, C_2H_6, $COC\ell_2$, $CH_3C\ell$, $CC\ell_4$, and $C\ell O$. It was found that only OCS, NO_2, and HNO_3 produce significant absorption near the measured lines of $C\ell O$.

A ground-based search for stratospheric chlorine monoxide was carried out during May and October 1981 with an infrared heterodyne spectrometer in the solar absorption mode. Analysis of those data was completed in 1982, and appeared in the scientific literature in 1983. Lines due to stratospheric nitric acid and tropospheric carbonyl sulfide were detected at about 0.2

percent absorptance levels, but the expected 0.1 percent lines of chlorine monoxide were not found. Analysis of the data implies that $C\ell O$ is less abundant by at least a factor of 7 than is indicated by insitu measurements. We find that the upper limit for the integrated vertical column density of chlorine monoxide is 2.3×10^{13} molecules per square centimeter at the 95 percent confidence level. These results imply that the release of chlorofluorocarbons may be significantly less important for the destruction of stratospheric ozone than is currently thought.

Improved sensitivity was achieved in 1982 and 1983, and observations taken in early 1983 suggest the presence of a very weak spectral line at the position expected for $C\ell O$. Its weakness is consistent with the upper limit determined earlier. Analysis and supporting laboratory measurements are continuing.

E. Journal Publications

"Infrared Heterodyne Spectroscopy of Seven Gases in the Vicinity of Chlorine Monoxide Lines," H. A. Weaver, M. J. Mumma, J. L. Faris, T. Kostiuk, and J. J. Hillman, Applied Optics 22, 1562 (1983).

"Is There Any Chlorine Monoxide in the Stratosphere?" M. J. Mumma, J. D. Rogers, T. Kostiuk, D. Deming, J. J. Hillman, and D. Zipoy, Science 221, 268 (1983).

D. AIRCRAFT-BORNE MEASUREMENTS

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NASA Ames

Summary of Upper Atmospheric Research

A. Title of Research Task: Tracer Studies in the Stratosphere

B. Investigators and Institutions:

E. C. Y. Inn	NASA (retired June 1982); currently guest worker at Ames.
James F. Vedder	NASA Ames
Estelle P. Condon	NASA Ames

C. Abstract of Research Objectives: Minor constituents play an important role in upper atmosphere photochemistry and serve as tracers in transport and mixing studies in troposphere-stratosphere exchange processes. These studies are essential to an understanding of the mechanisms by which minor constituents originating in the troposphere, both naturally occurring and anthropogenic, reach the stratosphere; data on tracer distributions thus acquired are important in the development of models for predicting photochemical effects in the stratosphere.

D. Progress and Results:

In Fiscal Year 1982, the value of CO as a tracer for exchange processes was demonstrated by Condon and Danielsen (unpublished) with data obtained in the underflight of the Space Shuttle by the CV-990 on November 13, 1981. Fortuitously, the collection of whole air samples for subsequent analysis coincided with a tropopause folding event over the ocean. The measured values of the mixing ratio of CO showed a deep penetration into the troposphere of stratospheric air low in CO, thus verifying a folding process occurring over the ocean that had previously been thought to be solely of orographic origin by some. Concentrated samples of stratospheric air collected for sulfur gas analyses under another program were subsequently analyzed for halocarbons and N_2O. By taking advantage of these flights, we obtained measurements of CF_2Cl_2, $CFCl_3$, CH_3Cl, and N_2O from April to December over a range of latitudes. Preliminary investigations of gas-chromatographic methods for determining the non-methane hydrocarbon content of these concentrated samples were undertaken.

In 1983, flame ionization and mass spectrometer detectors were used with gas-chromatographic separations of whole air and cryogenically concentrated samples to detect low parts per trillion levels of non-methane hydrocarbons. Analyses of stored residuals of samples collected on U-2 flights showed mixing ratios of ethane, ethylene, acetylene, and possibly propane in the low parts per trillion range.

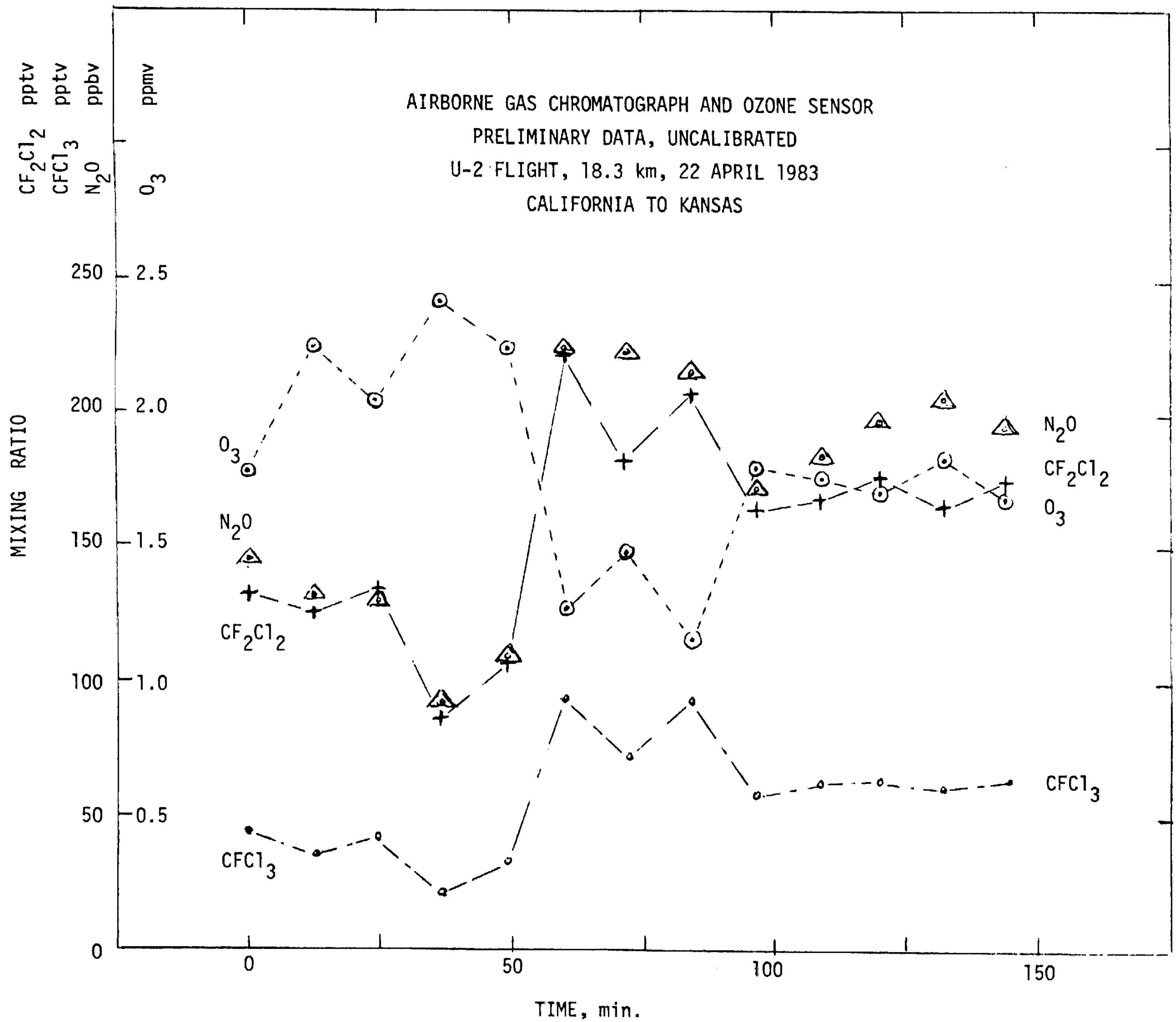
A special Metal Bellows pump for high altitude work is being procured for collection of pressurized whole air samples in the lower stratosphere for non-methane hydrocarbon analyses. A nondispersive infrared sensor for carbon monoxide developed by Beckman Instruments, Inc., for the Gasp Program was evaluated for possible use on the U-2 aircraft. An intercomparison on the CV-990 with collected samples of whole air analyzed subsequently in the laboratory for carbon monoxide by gas chromatography showed agreement within the precision of the measurements in most cases.

The airborne gas chromatograph and ozone monitor were carried on the multi-instrumented U-2 aircraft based in Topeka, Kansas, during the balloon intercomparison experiment. Preliminary results for the flight from Ames to Topeka at 18.3 km altitude showed good correlation between mixing ratios of CF_2Cl_2, $CFCl_3$, CCl_4, and N_2O and anti-correlation of O_3 with the first four species. Mixing ratios of N_2O and CF_2Cl_2 varied by factors of 2-1/2, $CFCl_3$ by 4-1/2, and O_3 by 2, during the flight. These variations are larger than expected, but the meteorological conditions prevailing along the flight path indicate that mixing processes associated with cyclonic and anticyclonic weather patterns were active at the time of the flight.

E. Journal Publications:

Vedder, J. F., E. C. Y. Inn, D. O'Hara, E. P. Condon, and R. F. Miranda, Measurements of CF_2Cl_2, $CFCl_3$, and N_2O during the 1980 Panama Water Vapor Exchange Experiment. EOS - Trans. Am. Geophys. Union, 62, 877, 1981 (Abstract).

Vedder, J. F., E. C. Y. Inn, D. O'Hara, E. P. Condon, and R. F. Miranda, Trace gas measurements during the NASA Water Vapor Exchange Experiment, edited by A. P. Margozzi, NASA TM 84297, 25-35, 1983.



AIRBORNE GAS CHROMATOGRAPH AND OZONE SENSOR
PRELIMINARY DATA, UNCALIBRATED
U-2 FLIGHT, 18.3 km, 22 APRIL 1983
CALIFORNIA TO KANSAS
CF_2Cl_2 pptv
$CFCl_3$ pptv
N_2O ppbv
O_3 ppmv
MIXING RATIO
TIME, min.
O_3
N_2O
CF_2Cl_2
$CFCl_3$
0
50
100
150
200
250
0.5
1.0
1.5
2.0
2.5

NASA Ames

NASA Ames

Title: U-2/ER-2 Meteorological Measurement System

Investigators: K. Roland Chan and Stanely G. Scott
M. S. 245-5
NASA Ames Research Center
Moffett Field, CA 94035

Objectives:

The U-2/ER-2 aircraft (NASA 706, 708, and 709) are to be equipped with special instrumentation to accurately measure the meteorological parameters (pressure, temperature, and 3-dimensional wind vector) during mission flights of Stratosphere and Climate Research programs. The meteorological measurement system (MMS) consists of an inertial navigation subsystem (INS), a pressure/temperature/air motion sensor subsystem, and a data acquisition subsystem.

Progress and Results

The funding of this task was initiated in FY 1983. The inertial navigation unit is the Litton LTN-72 model, which was purchased under the Airborne Missions and Applications Program.

Much of the pressure/temperature/air motion sensor subsystem was developed before FY 1983 under a separate task. The air motion sensors to measure the angle of attack (α) and the angle of sideslip (β) are mounted on a nose-boom. The existing pressure and temperature sensors are part of the resident aircraft instrumentation. A separate temperature and pressure subsystem, dedicated to meteorological measurements, has been designed.

An additional data acquisition subsystem, based on previous design, has been rebuilt, ruggedized, and improved (more digital electronics, better precision on pitch and roll measurements, more reliable internal clocks, etc.). A new analog signal processor, using intermediate digital electronics, has been designed and built in order to provide more accuracy and flexibility for vertical velocity computation and processing.

National Aeronautics and
Space Administration
Ames Research Center
Moffett Field, California
94035

NASA

Reply to
Attn of: SS:245-1 (APM)

20 Oct 1983

TO: EE-8/Robert T. Watson, Program Scientist

FROM: SS:245-1/Angelo Paul Margozzi, Technical Monitor

SUBJECT: Research Summary of Upper Atmospheric Research Task

REFERENCE: (a) Watson to Margozzi, dtd. 17 Oct. 1983

The letter of reference (a), requested the following subject summary:

A. ER-2 Experiment Integration

B. A. Margozzi, Ames Research Center

C. The nominal objectives are to integrate experiments in a timely fashion for missions, to provide flight support, and to provide auxiliary experiments as required to meet science objectives of the missions. This task was unfunded in FY'82 and funded,as a convenience, half way through FY'83 as a vehicle to fund two NOAA proposals.

D. The ozone, and F11, F12, and N2O Balloon Intercomparison Campaign flights were made in August 1983 at Palestine, Texas by Albritton and Proffitt, and Goldan, Kuster, and Albritton, respectively. The samples and data are being analyzed and compared.

E. No publications to date.

Angelo Paul Margozzi

Angelo Paul Margozzi

APMargozzi:xt 10-20-83/5517

25th Anniversary
1958-1983

E. ROCKET-BORNE MEASUREMENTS

UV SOLAR FLUX IN THE MESOSPHERE

J. E. Mentall and J. E. Frederick
NASA/Goddard Space Flight Center
Laboratory for Planetary Atmospheres
Greenbelt, Maryland 20771

Abstract:

Measurements are made of the solar ultraviolet flux transmitted in the mesosphere using a pointed double pass spectrometer suspended from a high altitude parachute. The parachute is deployed from an Orion rocket and data is obtained over the altitude range 65-35 km. The prime goal of this experiment is to verify absorption cross sections for the O_2 Schumann-Runge bands by comparing the observed attenuation in the mesosphere with that calculated using absorption cross sections measured in the laboratory.

Summary of Progress:

A flight using the prototype version of the experiment took place in October, 1980. Data obtained in this flight were used to verify O_3 absorption cross sections in the Hartly Continuum and to obtained accurate solar irradiances over the wavelength range 200-330 nm. However, the signal-to-noise ratio was not sufficient to obtain accurate measurement below 200 nm in the Schumann-Runge region. Experience gained in the first flight was used to redesign the pointing which in turn allows the experiment to be flown without a transmission diffuser which increases the signal by a factor of 100. The new system was flown on August 3, 1982 but was unsuccessful when three of the four interpanel hem tapes on the parachute tore shortly after deployment of the parachute. Consequently, the pointing system did not acquire the sun until falling to 40 km which prevented the main objective of the experiment from being obtained. However, data from the flight support the conclusion that the experiment would have achieved all its goals had the parachute functioned normally. The parachute has been improved and the experiment will be reflown in Summer, 1984.

Publications:

"The Solar Irradiance from 200-330 nm", J. E. Mentall, J. E. Frederick, and J. R. Herman, J. Geophys. Res., 86, 9881, 1981.

UV ABSOLUTE FLUX AND VARIABILITY

J. E. Mentall and D. E. Williams
NASA/Goddard Space Flight Center
Laboratory for Planetary Atmospheres
Greenbelt, Maryland 20771

Abstract of Research Objectives:

The objective of this experiment is to determine the variability of the Sun over the 12 year solar cycle in the ultraviolet portion of the spectrum (160 to 350 nm). To achieve this, solar irradiance measurements are made using rockets as an observing platform on a yearly basis. Short term variations in the Sun's output are accounted for using measurements from the Scanning Backscattered Ultraviolet (SBUV) experiment on Nimbus-7. The rocket measurements also provide a basis for determining long term degradation of the SBUV sensitivity and re-establishing its calibration.

Summary of Progress and Results:

Calibration procedures have been enhanced by using improved design of calibration test fixtures, new microcomputer controlled Ground Support Equipment to facilitate reducing calibration data, and the acquisition of a number of NBS calibrated standard lamps for cross reference. With the current state-of-the-art the experiment accuracy should approach $\pm 5\%$.

A new experiment payload containing three 0.125 meter focal length spectrometers to cover the region from 140 to 350 nm was designed, tested, calibrated, and integrated into a Taurus-Orion rocket this past year. An attempt was made to launch this experiment from White Sands, New Mexico on July 25, 1983. The launch was unsuccessful due to a vehicle failure which prevented the rocket from reaching the proper altitude. Preliminary results from the failure analysis indicates that premature nose cone deployment and the subsequent pressure build up caused the payload to break away from the Orion second stage. Fortunately the payload was recovered with only minor damage.

The experiment has been refurbished, recalibrated, and will be flown on a Black Brandt as part of a Solar Constant Experiment. Launch of this rocket is to coincide with the flight of Spacelab I and provide coincident measurements with the solar spectrometer on Spacelab as well as with SBUV.

Irradiance measurements in the 150 to 200 nm region from three previous rocket flights have been reduced to final form and a paper describing the results submitted for publication. Good agreement is observed between these measurements and the recent flight of Mount and Rottman as well as with the initial irradiance measurements from Nimbus-7. At 150 nm, however, only a 30% variation was observed with solar activity which is in contrast to the factor of two observed by Mount and Rottman.

Publications:

"The Solar Spectral Irradiance from 150 to 200 nm", J. E. Mentall, B. Guenther, and D. E. Williams, J. Geophys. Res., (submitted).

Measurement of Solar Spectral Irradiance at Wavelengths between 1200 and 4000 A

George H. Mount* and Gary J. Rottman
Laboratory for Atmospheric and Space Physics
University of Colorado
Boulder, Colorado 80309

Abstract of Research Objectives:

The objective of this study is to measure the solar absolute UV irradiance incident on the Earth's atmosphere using instruments launched on rockets. The instruments are calibrated at NBS-SURF and have absolute calibrations of approximately ± 10%. We began this study at solar maximum and are planning to continue with two measurements per year (one piggybacked and one dedicated) through the launch of VARS.

Summary of Progress and Results:

Results from the flights of this study (June, 1979; July, 1980; May, 1982; January, 1983; and July, 1983) indicate an significant enhancement of irradiance below 1900 A during solar maximum. The enhancement is approximately a factor of two of Lyα and is within the error bars of the experiment above 1900 A. Significant improvements have been made since 1979 in the quality of the absolute calibration. This has been primarily achieved through use of the NBS-SURF facility.

Thus, the measurements achieved in this study provide the first set of systematic absolutely calibrated data of the variability of the solar UV irradiance over a significant portion of the cycle from solar maximum to solar minimum.

Journal Publications:

Mount, G., Rottman, G., and Timothy, J.: 1980, JGR 85, 4271. The Solar Spectral Irradiance 1200-2550 A at Solar Maximum.

Mount, G. and Rottman, G.: 1981, JGR 86, 9193. The Solar Spectral Irradiance 1200-3200 A, July, 1980.

Mount, G. and Rottman, G.: 1983, JGR 88, 5403. The Solar Absolute Spectral Irradiance 1150-3173 A: 17 May 1982.

Mount, G. and Rottman, G.: 1983, JGR 88, 6807. The Solar Absolute Spectral Irradiance 1150-3173 A: 12 January 1983.

Mount, G. and Rottman, G.: 1983, JGR, in preparation. The Solar Absolute Spectral Irradiance 1150-3173 A: 25 July 1983.

*Current address: Code 4141.5
Naval Research Laboratory
Washington, DC 20375

A. Title of Research Task

Intercomparison Measurement Between Rocket/Borne and Balloon/Borne Chemiluminescent Payloads

B. Investigators and Institutions

Jack J. Horvath
University of Michigan
Dept. of Atmospheric and Oceanic Science
College of Engineering
2455 Hayward
Ann Arbor, Michigan 48105

C. Abstract of Research Objectives

The majority of the existing in-situ measurements of the nitric oxide mixing, in the altitude region 30-40 km., were obtained by two groups, i.e., Ridley and his co-workers at York University and the group at the University of Michigan. The internal consistency within each group's data set appears to be quite good. However, there is a clear disparity in the absolute magnitude between the data sets, a difference by a factor of two. The research effort undertaken here was initiated with the specific purpose of resolving this disparity.

D. Summary of Progress and Results

A laboratory intercomparison between the balloon and rocket borne NO payloads was carried out during the week of 19 April 1982 at York University in Downsview, Ontario. The practical results from this effort were limited by the fact that neither payload could be, at this time, subjected to stratospheric conditions such that real payload functions could be employed exactly as they take place during a rocket and/or balloon flight, e.g., background calibration sequences, etc. We did, however, resolve (a) that the reference gas (NO/N_2) sources between the respective laboratories is in good agreement, (b) that the Michigan instrument sensitivity can be derived accurately in terms of the variable instrument parameters and (c) that we were not able to resolve the key question relating to the factor of two discrepancy between the data reported by Ridley et-al which resulted from the balloon payloads and the data obtained from the Michigan payloads in the altitude region 30-40 km.

The implementation of a rocket-balloon intercomparison flight was discussed with Dr. Ridley, as well as Dr. Albritton at NOAA, and although there seems to be complete agreement as to the practicality of undertaking a comparison flight it apparently is not very high on their priority list for things to carry out in the near future. The latest estimate, as imagined by the NOAA group, would put the comparison flight into the 1984 calendar year.

In the meantime we have carried out a research effort which was directed toward reviewing the credibility of the rocket borne instrument. To this end one payload was instrumented with an on-board NO calibration device for the purpose of in-flight calibration. A flight of this instrument was carried out on 13 January 1983. The in-flight calibration results were extremely successful and very definitely show that the calculated sensitivities as derived from the instrument parameters during a rocket flight are quite good, e.g., the predicted in-flight calibration mixing ratio was evaluated to be 39.6 ± 1.6 PPBV which compares extremely well with the expected value, based upon flow dilution, of 40.1 ± 3.2 PPBV. The results of the in-flight calibration experiment were presented at the 1983 Spring AGU meeting.

On the basis of the January rocket flight we can conclude:

1) that the method of predicting instrument sensitivities as employed by the rocket borne instrument is not responsible for the discrepancy in the respective NO mixing ratio data sets.

2) that we are not losing ambient NO molecules during their transit in our instrument inlet tube due to adsorbtion and/or possible reaction with other minor constituent gases since the NO cal. gas was injected within .625 cm. from the entrance of the 75 cm. long inlet tube and thereafter travel the same path as the ambient molecules.

3) that we now have some indirect evidence that the measured ozone generated background level as derived during a flight experiment is representative of the true background level (the scheme for determining the ozone generated background signal during a rocket flight could be investigated for credibility, in the laboratory, by the adding of a low cost Roots Blower to our calibration station).

The research activities described above should add credibility to the pending rocket/balloon intercomparison flight and a future laboratory investigation of the ozone generated background signal, as derived by the rocket payload, would make the comparison more meaningful.

E. Journal Publications

Horvath, J.J., J.E. Frederick, N. Orsini, and A.R. Douglass, Nitric oxide in the upper stratosphere: measurements and geophysical interpretation, J. Geophys. Res., in press 1983.

Sounding Rocket Studies of N_2O, NO, and Other Trace Constituents in the Upper Stratosphere and Mesosphere Using Cryogenic Grab Sampling Techniques

E. C. Zipf and P. W. Erdman
Department of Physics and Astronomy
University of Pittsburgh
Pittsburgh, PA 15260

ABSTRACT

A cryogenic whole-air sampler is used to investigate the sources and sinks of CO_2, N_2O, NO, CH_4, and other minor constituents in the middle atmosphere from 40-75 km. The atmsopheric samples are collected on gold-plated surfaces maintained at $\sim$15° K by CTI-8 Sterling refrigerators. The cold fingers are located in specially prepared stainless steel canisters and are exposed to the atmosphere through pneumatically actuated valves. Three successful rocket flights from the White Sands Missile Range have obtained large samples ($\sim$4 std-liters) in this altitude range. The samples are concentrated further after recovery so that the density of the final samples analyzed by optical, mass spectrometer, and gas chromatograph techniques are $\sim 10^5$ times the ambient stratospheric values. CO_2, CH_4, and N_2O profiles have been obtained from these flights, and the fluorocarbon content of these samples is being evaluated currently.

A cryogenic whole-air sampler is being developed by the University of Pittsburgh in order to investigate the sources and sinks of CO_2, N_2O, NO, CH_4, and other minor constituents in the middle atmosphere from 40-75 km. These measurements complement balloon and high-altitude aircraft studies at lower altitudes and provide truth-test data for remote-sensing satellite experiments and boundary condition information for model atmosphere calculations. The [CWAS] payload uses CTI-8 refrigerators to cool four-pound, gold-plated copper blocks to $\sim$15° K. These cold fingers are located in specially prepared stainless steel chambers which are sealed by pneumatically actuated valves with a throat cross-sectional area of 11.4 cm^2. The valves are opened at predetermined altitudes by the on-board telemetry timers. The samples obtained in this manner are quite large ($\sim$4 std-liters) and are concentrated further upon recovery. Optical, mass spectrometer, and gas chromatograph techniques are used to analyze the samples which are $\sim 10^5$ times as dense as their initial stratospheric value.

An initial engineering flight of the [CWAS] payload was carried out on 9 August 1982 from the White Sands Missile Range. High quality samples were obtained between 49-63 km and valuable engineering data on the effects of vehicle angle of attack on the sample size and integrity were obtained.

The CO_2, CH_4, and N_2O samples did not appear to be compromized by vehicle outgassing, but a significant enhancement in the H_2O density was observed. In order to minimize this problem, the sampling orifices were redesigned to attach the shock wave farther in front of the vehicle, and additional vents were added to depressurize the payload (telemetry, parachute, etc.) more quickly.

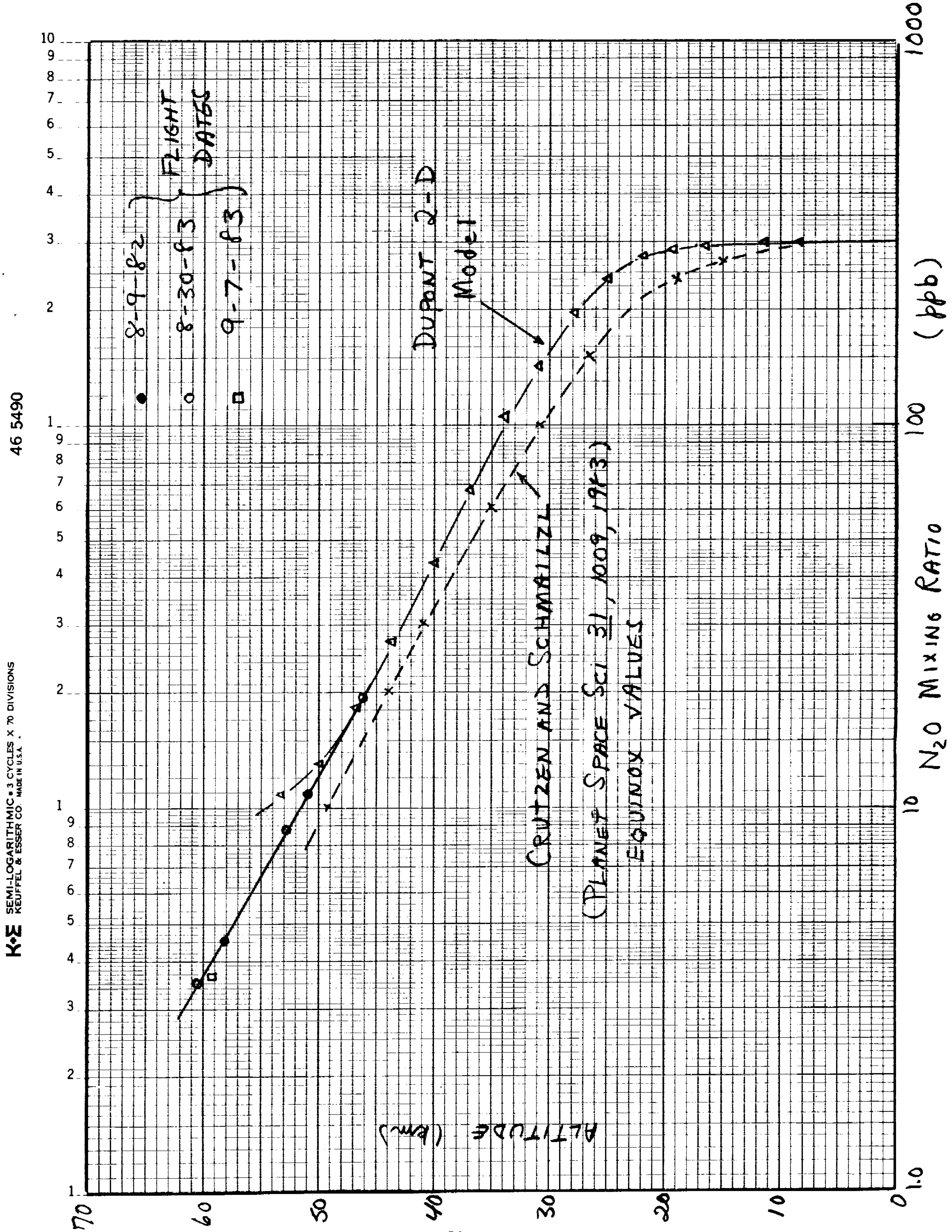
Two additional engineering flights were carried out on 30 August 1983 and 7 September 1983. The first flight obtained samples from 46-61 km while the second rocket was designed to explore how high in altitude the [CWAS] might work. The flights were highly successful. In particular, the new sampling orifices dramatically reduced the H_2O outgassing problem. Our preliminary analysis suggests that the [CWAS] technique may provide a viable method for water vapor measurements above 40 km. Excellent N_2O, CH_4, and CO_2 samples were obtained. No statistically significant variation in the CO_2 mixing ratio between 40-61 km was observed, and a preliminary value of 327 ppm was obtained. Work continues on the N_2O and fluorocarbon profiles from these flights. The methane results, which agree quite well with those adopted by Crutzen and Schmailzil (Planet. Space Sci 31, 1009, 1983) are listed below

Z (km)	CH_4 Mixing Ratio	Flight Date
46.7	0.41 ppm	8-30-83
51.0	0.31	8-09-83
53.0	0.30	8-30-83
58.3	0.235	8-09-83
59.4	0.225	9-07-83
60.3	0.225	8-30-83

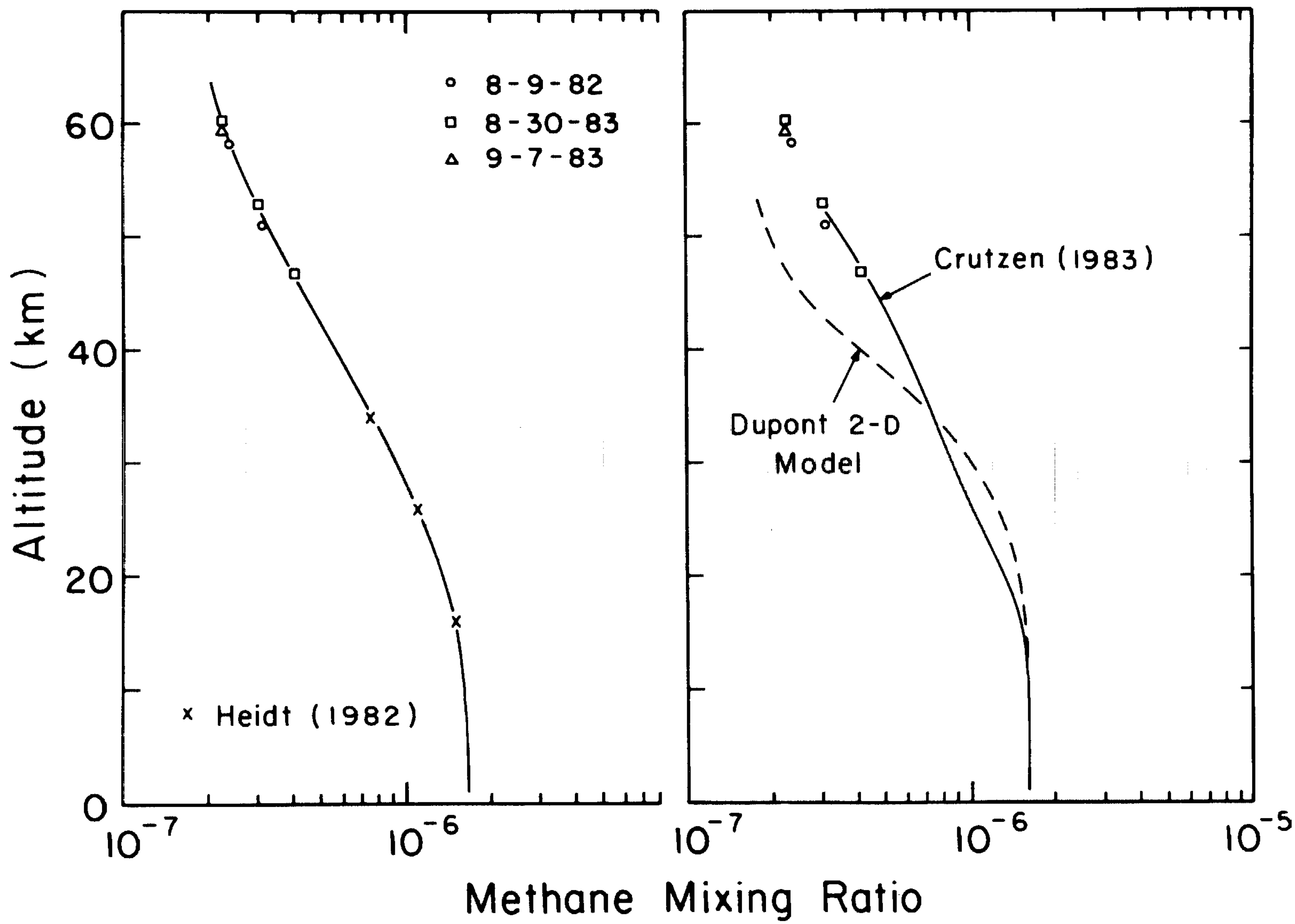
Finally, we must note that one serious misfortune marred the September 9, 1983 flight. During re-entry, the payload landed on an exceedingly hard gypsum surface and was badly damaged. Repairs are underway in preparation for sampling studies in the auroral zone during February 1984.

CAPTIONS

CH_4 and N_2O data obtained above 40 km by a cryogenic whole-air sampler. The results are compared with a 2-D model provided by Dupont and with the N_2O and CH_4 profiles adopted by Crutzen and Schmailzl (Planet. Space Sci. 31, 1009, 1983) in a recent stratospheric model. The flight dates are noted in the figures.



K+E SEMI-LOGARITHMIC • 3 CYCLES X 70 DIVISIONS
KEUFFEL & ESSER CO. MADE IN U.S.A.
46 5490
8-9-82
8-30-83
9-7-83
FLIGHT DATES
DUPONT 2-D Model
CRUTZEN AND SCHMAILZL
(PLANET SPACE SCI 31, 1009, 1983)
EQUINOX VALUES
N_2O MIXING RATIO (ppb)
ALTITUDE (km)
1.0
10
100
1000
70
60
50
40
30
20
10
0



8-9-82
8-30-83
9-7-83
Heidt (1982)
Crutzen (1983)
Dupont 2-D Model
Altitude (km)
Methane Mixing Ratio

IN SITU OZONE SOUNDINGS

Principal Investigator: Ernest Hilsenrath
Code 964
Atmospheric Chemistry Branch
NASA/Goddard Space Flight Center
Greenbelt, MD 20771

Abstract

This research task has been directed toward in situ observations from balloons and rockets. The major efforts are: final analysis of chemiluminescent rocket sounding data in support of satellite observations, analysis of balloon soundings for climatological studies, and the organization of the Balloon Ozone Intercomparison Campaign (BOIC). In the first effort, research using the chemiluminescent rocket sounding measurement has been completed, and this system is now retired. The second is an on-going effort to develop a climatology of lower stratospheric ozone, and the third is a new effort to determine the accuracy and precision of several types of ozone measurements taken from a balloon.

Summary of Progress and Results

All data taken by the rocket chemiluminescent sonde have been processed and analyzed. Nearly all the data have either been published in the open literature or turned over to the satellite investigators (SBUV, LIMS, SME) when data have been taken for satellite comparisons. A draft report on the results of the International Ozone Rocket Intercomparison have been submitted to the organizers and partial results published in Advances in Space Research. In this paper, we showed how combined satellite and rocket data could be used to describe ozone variations. It was shown that ozone at the 5 mb level was controlled by transport. Rocket data have also appeared in JGR and Science. In the most recent study (JGR in press) comparisons with SAGE satellite data with balloons and chemiluminescent rocket data show mean differences of 10% in the lower stratosphere and 13% in the upper stratosphere.

In the effort to refine the climatology of lower stratospheric and tropospheric ozone, equatorial balloon soundings from Natal, Brazil, were analyzed for seasonal variability using a two-year data set. Tropospheric ozone was found to be 30% higher than previously published data in the equatorial region. This result may in part be instrumental but can also be correlated with a regional difference in total ozone which has been detected in satellite data. These results have been published in JGR.

The Balloon Ozone Intercomparison Campaign (BOIC) is now underway. The objective of BOIC is to determine the accuracy and precision of the "operational" ozone sounders and techniques under development. The longer range goal is to identify a system which can be used routinely on a balloon to 40 km with an accuracy of better than 5%. The instrument could then be used on research

In Situ Ozone Soundings
(P.I. Ernest Hilsenrath)

balloons and for intercomparisons with satellite ozone measurements. The campaign involves 11 investigators from NASA, other government agencies, Germany and Canada. A portion of the flight campaign was conducted in July 1983 and completion is expected by October, with the reflight of the multiple instrument gondola. A data base consisting of all ozone profiles taken during BOIC is being set up at GSFC. This will allow easy access of the data by the investigators. An objective procedure for interpreting the intercomparison data using the data base is being developed.

Journal Publications

Hilsenrath, E., Ozone variations observed during the international ozone rocketsonde intercomparison, Adv. Space Res., 3, No. 7, 1983.

Klenk, K., P. K. Barhtia, and E. Hilsenrath, Standard ozone profiles from balloon and rocket data sets, J. Climate App. Met., (in press) 1983.

Kirchhoff, V. and E. Hilsenrath, Equatorial ozone characteristics as measured at Natal (5.9°S, 35.2°W). J. Geophys. Res., 88, 1983.

McCormick, P., R. Jurisler, E. Hilsenrath, A. Krueger, and M. Osborne, Satellite and correlative measurements of stratospheric ozone: Comparison of measurements made by SAGE, ECC balloons, chemiluminescent and optical rocket sondes, J. Geophys. Res. (in press) 1983.

A. TITLE OF RESEARCH TASK

Rocoz System Improvement

B. INVESTIGATORS AND INSTITUTIONS

Alfred C.Holland
Laboratory for Planetary Atmospheres
Goddard Space Flight Center
Wallops Flight Facility
Wallops Island, Virginia 23337

C. ABSTRACT OF RESEARCH OBJECTIVES

The primary objective of the Correlative Measurements Program is to obtain ozone vertical profiles in the stratosphere of sufficient accuracy and precision to provide an independent check on the validity of the profiles from satellite-borne ozone sensors. The Rocket Optical Ozone Sonde (Rocoz) is a key element of such correlative measurements. This task addresses the improvement of the accuracy, precision, and reliability of the Rocoz system. In the past year the integration, testing, and calibration of the Rocoz hardware and the data reduction and analysis have been consolidated at the Wallops Flight Facility. Filter specification and characterization have been improved; the radiometric calibration is now absolute and tied to NBS standards.

D. SUMMARY OF PROGRESS AND RESULTS

Successful efforts have been directed toward establishment of adequate calibration facilities at GSFC and WFF, study of the interplay between spectral solar flux and the effective ozone absorption coefficients, and examination of the data reduction and analysis programs. Specifically:

1. Equipment for absolute radiometric calibration at ultraviolet wavelengths has been set up at the GSFC calibration facility and checked versus NBS standards.

2. Calculation of the effective absorption coefficient for each UV channel has been revamped. Sensitivity coefficients of the effective absorption coefficient to errors in the solar flux, ozone absorption coefficients, and filter center wavelength have been derived.

3. New specifications for the filters have been chosen that increase the signal-to-noise ratio of the payload by a factor of 20 and reduce the gain spread between UV channels to a ratio of less than 2.0 with only a slight reduction in the maximum altitude for useful data.

4. All data reduction and analysis procedures and programs have been carefully examined and are now consolidated on the Data General Eclipse computer operated by the Applications Directorate at WFF.

5. Transmittance calibration of the Cary-17 dual-beam spectrophotometer has been accomplished using standards traceable to NBS. The Cary has now been linked to the Eclipse computer via a small PDP-1103 computer.

6. The flight test of the new payload and procedures, August 23, 1983, verified the projected improvements; signal-to-noise ratio from the Rocoz photometer increased by at least an order of magnitude from prior flights; the signal for full sunlight for the UV channels were each within 5 - 9% of the predicted signal; ozone profiles from the four filters agree within 2.5%

E. JOURNAL PUBLICATIONS

"Validation of the BUV Satellite Ozone Sensor Using the Rocket Ozonesonde," R.W.L. Thomas, W.A. Pearce, A.C. Holland and D.U. Wright, Applied Optics, 21, 2435-2441, July 1982.

"The Linearity of BUV Observations with Respect to Measures of the Vertical Ozone Profile, R.W.L. Thomas, A.C. Holland, Applied Optics, submitted for publication.

F. BALLOON FACILITIES

MULTI-SENSOR BALLOON MEASUREMENTS

Wesley T. Huntress, Jr.
Jet Propulsion Laboratory

In Fiscal 1983 the objectives of this program were to complete the construction of a new multi-instrumented, modular balloon gondola, and to modify an earlier multi-instrumented gondola, to support a second Balloon Intercomparison campaign to be conducted in Spring 1983 from the National Scientific Balloon Facility in Palestine, Texas. In addition, the JPL Balloon Flight Support group was to supply logistical assistance and ground-based equipment to support telemetry for the entire complement of balloon payloads to be flown on the international campaign. Following the Spring flight, the gondolas and ground-based equipment would be used for future multi-instrumented flights in the stratospheric science program.

The gondolas and GSE were constructed and the intercomparison campaign was conducted in late Spring. The first JPL gondola carried the JPL High Speed Interferometer (C. B. Farmer), the SAO Far-IR Interferometer (W. Traub), a Canadian IR Interferometer (W. Evans), a French IR Grille spectrometer (N. Louisnard) and a GSFC UV flux spectrometer (J. Mentall). The second JPL gondola carried the JPL Microwave Limb Sounder (J. Waters), the Denver University IR Emission Interferometer (D. Murcray) and the JSC ozone monitor (D. Robbins). After an initial aborted attempt in May, both gondolas flew in June and conducted nominal flights until termination. The gondola systems and ground-support equipment worked perfectly during flight. All instruments were supported well by the gondolas, and with only one exception each instrument returned atmospheric science data. The second JPL gondola returned to the ground safely, but the first separated from its parachute at termination and was destroyed with all instruments after free-fall. Investigation of the cause is underway.

NASA UPPER ATMOSPHERIC RESEARCH
BALLOON PROGRAM SUPPORT
FY'82 AND FY'83

Provided SR&T support for the UAR Program through management of the NASA Balloon Program which, as of October 1, 1982, includes management of the National Scientific Balloon Facility.

During FY'82, 25 balloon flights were conducted for NASA sponsored UAR scientists as follows:

Experimenter/Organization	Number of Flights	Location
Hofmann/Wyoming	11	Laramie, WY
	1	Laredo, TX
	1	Sinton, TX
Berg/NCAR	2	HAFB, NM
Anderson/Harvard	2	Palestine, TX
Mauersberger/Minnesota	1	Palestine, TX
Farmer/JPL	1	Palestine, TX
Holzworth/Washington	1 Tethered Balloon	Wallops Island, VA (3 days)
Watson/NASA HQ BIC SERIES		
BIC Gongola 2 -		
Pommereau/CNRS, France Igawa/Tokyo, Japan Murcray/Denver, U.S. Bennetti/IROE-CNR, Italy Roscoe/Oxford, U.K. Woods/NPL, U.K.	1	Palestine, TX
BIC Gondola 3 - Zander/Liege, Belgium	1	Palestine, TX
BIC Gondola 4 - Waters/JPL, U.S. Murcray/Denver, U.S. Robbins/JSC, U.S.	1	Palestine, TX
BIC Gondola 5 - Evans/AES, Canada	1	Palestine, TX
Murcray/Denver	1	HAFB, NM

Thus far in FY'83 (October 1982 thru September 14, 1983), 28 balloon flights have been conducted for NASA sponsored UAR scientists as follows:

Experimenter/Organization	Number of Flights	Location
Watson, Woods/NASA HQ, U.S. NPL, U.K. (Reflight of 1982 UAR BIC Gondola 2)	1	Palestine, TX
Hofmann/Wyoming	12	Laramie, WY
Heaps/GSFC	1	Palestine, TX
Huntress, Traub/JPL, Smithsonian	1	Palestine, TX
Holzworth/Washington	2 Tethered Balloon	Wallops Island, VA (2 days each)
Thomas/Colorado	1	Palestine, TX
Watson/NASA HQ UAR BIC SERIES		
BIC Gondola 2 - Woods/NPL, U.K.; Roscoe/Oxford, U.K.; Pommereau/CNRS, France; Kerr/AES, Canada; Ogawa/Tokyo, Japan; Murcray/Denver, U.S.	1	Palestine, TX
BIC Gondola 1 - Farmer/JPL, U.S.; Traub/Smithsonian, U.S.; Roscoe/Oxford, U.K.; Louisnard/Onera, France; Mentall/GSFC, U.S.; Evans, AES, Canada	1	Palestine, TX
Hofmann/Wyoming	1	Palestine, TX
Watson/NASA HQ UAR BIC SERIES		
Watson, Woods/NASA HQ, NPL (Reflight of BIC Gondola 2)	1	Palestine, TX
Watson, Farmer/NASA HQ, JPL (Reflight of BIC Gondola 1)	1	Palestine, TX

Experimenter/Organization	Number of Flights	Location
BIC Gondola 3 -	1	Palestine, TX
Zander/Liego, Belgium		
Evans/AES, Canada		
BIC Gondola 4 -		
Waters/JPL, U.S.	1	Palestine, TX
Murcray/Denver, U.S.		
Robbins/JSC, U.S.		
Hilsenrath, Watson/GSFC, NASA HQ		
UAR BOIC SERIES		
Weinstock/Harvard	1	Palestine, TX
Proffitt/NOAA		
Robbins/JSC		
Ainsworth/GSFC		
Holland/GSFC/WFF		
Mentall/GSFC		
Komhyr/NOAA		
Torres/GSFC/WFF		
Evans/AES, Canada		
Attmanspacher/Germany		
BOIC Gondola 2 -		
Mauersberger/Minnesota	1	Palestine, TX
Robbins/JSC		
Komhyr/NOAA		
Torr/Utah State University	1	Palestine, TX

G. INSTRUMENT DEVELOPMENT

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SUMMARY FOR NASA PROGRAM

A. Title of Research Task:

"Ground-Based Feasibility Testing of Laser Remote Sensing Using Infrared Differential Absorption"

B. Investigators and Institutions:

D. K. Killinger, N. Menyuk, and A. Mooradian; Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, MA 02173-0073

C. Abstract of Research Objectives:

The objective of this program is to experimentally determine the system requirements for laser remote sensing of trace constituents and ambient species in the atmosphere. The effort includes the ground-based feasibility testing of a CO_2 laser differential-absorption LIDAR (DIAL) system, the investigation of detection ranges and sensitivity, and the demonstration of the remote-sensing of selected species in the atmosphere. Emphasis of the program has been on technology development with the eventual transfer of the technology to NASA laboratories.

D. Summary of Progress and Results (FY82-FY83):

During the FY82-FY83 time period, progress and accomplishments include:

(1) development of a pulsed, single-frequency CO_2 laser source and a dual-CO_2-laser, heterodyne-detection, differential absorption LIDAR system,

(2) measurement of the S/N ratios and detection ranges of the LIDAR system,

(3) experimental comparison of heterodyne and direct-detection DIAL measurements, and

(4) development of a tunable, pulsed Co:MgF_2 laser source and initial construction of a Co:MgF_2 DIAL system.

E. Journal Publications (FY82-FY83):

1. "Limitations of signal averaging due to temporal correlations in laser remote-sensing measurements,"
N. Menyuk, D. K. Killinger, and C. R. Menyuk, Appl Opt. 21, 3377 (1982).

2. "Limitations of laser transmission measurements due to correlated atmospheric effects,"
N. Menyuk and D. K. Killinger, SPIE Vol. 410 - Laser Beam Propagation in the Atmosphere, p. 32 (1983).

3. "Experimental comparison of heterodyne and direct detection for pulsed differential absorption CO_2 LIDAR,"
D. K. Killinger, N. Menyuk, and W. E. DeFeo, Appl Opt. 22, 682 (1983).

4. "Assessment of relative error sources in IR DIAL measurement accuracy,"
N. Menyuk and D. K. Killinger, Appl. Opt. 22, 2690 (1983).

Research Task: ECC Radiosonde Altitude Error Reduction

Investigator: C. L. Parsons, NASA Goddard Space Flight Center, Wallops Flight Facility

Abstract:

Pressure sensors on balloon-borne radiosondes are routinely utilized by NASA, the National Weather Service, and many other agencies to relate concurrent atmospheric measurements to the pressure-derived altitudes. Errors in the measured pressures contribute directly to errors in the calculated vertical distribution of atmospheric parameters including temperature, humidity, ozone, and wind velocity and direction. The objective of this study was to evaluate the accuracy of commercially available pressure sensors by comparing their derived altitudes with reference altitudes determined by C-Band radars. The balloon-borne sondes were launched at NASA's Wallops Flight Facility (WFF) and continuously tracked during their ascents by WFF C-Band radars.

Summary of Progress and Results:

The synoptic radiosonde uses an aneroid cell-baroswitch assembly as its pressure sensor. After undergoing appropriate tests to "age" the materials in the cell until an equilibrium is reached, the cells are calibrated in the laboratory. The calibration record is then included with the hardware when sold by the manufacturer. During the testing and calibration procedures, it is possible for the manufacturer to cull out those units that exhibit the most stability and hence which are most accurately calibrated; these are hereafter referred to as the <u>premium</u> baroswitch sensors. The remaining units are labelled as <u>standard</u> baroswitches. The third type sensor involved in this study was <u>the hypsometer</u>. In contrast to the aneroid cell devices, which expand as the pressure to which they are subjected is reduced, the hypsometer is based upon the relationship between the boiling point of a liquid and the ambient pressure. For stratospheric applications, the hypsometer is appealing because its altitude sensitivity increases with decreasing pressure in contrast to the aneroid cell sensors.

The radiosonde flights were launched from Wallops Island during two separate campaigns. During September and October 1982 the standard radiosondes were launched and in December 1982 - February 1983, the premium aneroid cell baroswitch sensors and hypsometers were flown. For each launch, two radiosondes were attached to a narrow platform 15.3 m beneath the balloon. They were separated by 1.8 m, midpoint-to-midpoint. A radar reflector was suspended an additional 4.6 m below the sondes. For the first series of flights using standard aneroid cell-baroswitch sensors, nineteen (19) sets of usable data were collected; a total of twenty-six (26) radiosondes were released in the second series.

Comparisons of the performance of the premium cells and hypsometers with the standard cells can best be made statistically. Table 1 contains the standard deviations of the sonde-radar differences at 5 km height intervals for each pressure sensor. The results for the standard cell agree closely with published results. It is obvious that the culling process does produce sondes whose aneroid cell behavior at low pressures is superior to that of the standard cell. It is also obvious that in the stratosphere, the hypsometer is clearly the preferred pressure sensor. With its standard deviation of 179 m at 35 km, it agrees with the radar heights to within the error bounds of the radar measurement.

Journal Publications:

Parsons, C. L., G. A. Norcross, and R. L. Brooks (1983), "Radiosonde Pressure Sensor Performance Evaluation Using Tracking Radars," submitted to J. Geophys. Res.

Table 1. Sonde-Minus-Radar Standard Deviations.

ALTITUDE	STANDARD BAROSWITCH		PREMIUM* BAROSWITCH		HYPSOMETER	
(km)	No. Obs.	1σ (m)	No. Obs.	1σ (m)	No. Obs.	1σ (m)
35	4	1838	19	742	16	179
30	14	605	22	322	20	117
25	19	258	24	167	22	122
20	19	139	20	134	22	92
15	19	91	24	118		
10	19	48	24	56		
5	19	30	24	32		

* Two anomalous baroswitch sondes were edited prior to this computation.

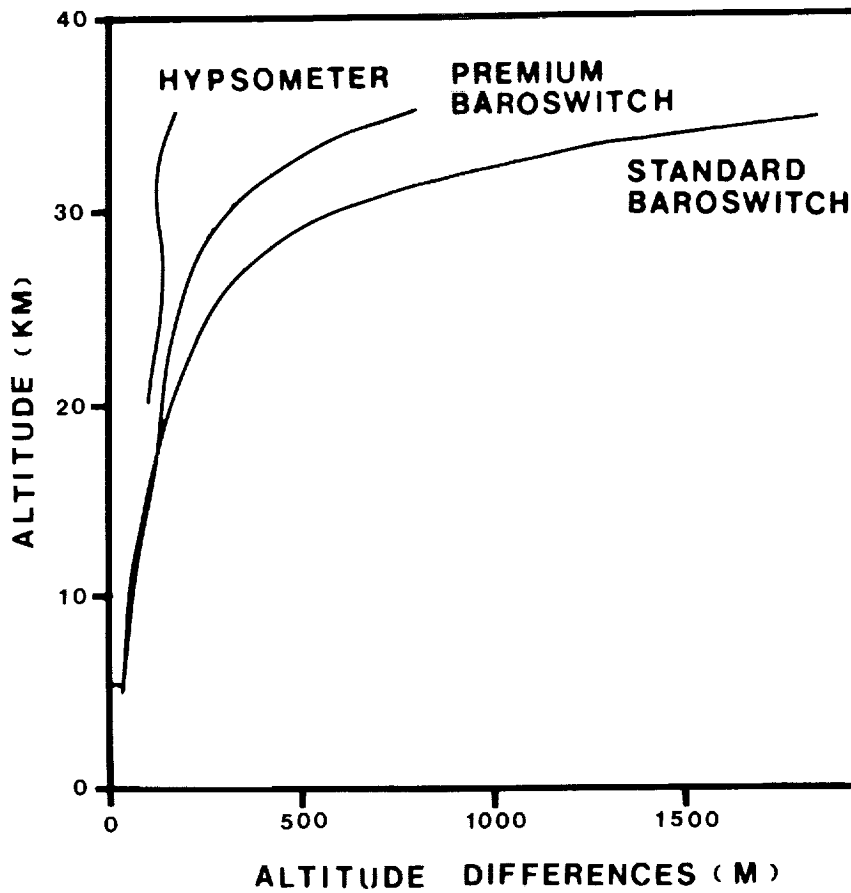

Figure 5 - Rms Differences Between Sonde-Derived Altitude and Radar Altitude for Each Type Sonde Tested.

A. Title: Solar Extinction Radiometry

B. Investigators and Institutions:

Principal Investigator (Instrument concepts)	J. H. Goad, Jr. NASA LaRC
Principal Investigator (Spectroscopic analysis and interpretation of balloon data)	Dr. Aaron Goldman University of Denver
Principal Investigator (Balloon measurements)	Dr. D. G. Murcray University of Denver

C. Abstract:

The objective of this research is to develop, demonstrate, and combine instrumental, experimental, and theoretical studies needed to better understand the capabilities of solar extinction radiometry. The data derived from this research are used to develop advanced satellite solar extinction radiometry to measure various atmospheric aerosols and gas species from the occultation geometry. SAM II and SAGE have provided data that establish this technique for global measurements of the vertical profile of aerosols and gaseous species (O_3 and NO_2). Research data and techniques developed under this program are essential to specify channel locations, bandwidths, throughputs, and error budgets for new satellite sensors (e.g., SAGE II). Data obtained from a high-altitude balloonborne instrument that simulates the satellite solar occultation geometry are being analyzed for the spectral identification of gas species and for their concentrations. Advanced techniques are being examined to extend existing and new space hardware for the measurement and retrieval of species such as OH, ClO, NO_3, SO_2, O_3, CS_2, and HNO_2. Also, this research requires development of data inversions, photochemistry models versus occultation geometry, and theoretically-compiled synthetic spectra. On other programs, these data are used to establish conceptual hardware designs for spacecraft instruments.

D. Summary:

High resolution solar spectra at high and low sun angles in the 3200-3400 Angstrom region were obtained during balloon fhights on February 9, 1977 (altitude of 41 km) and February 17, 1977 (altitude of 29 km). These data were analyzed using a layer-by-layer differential absorption method. This work demonstrates that high resolution UV spectra can yield accurate ozone volume-mixing ratios (Ref. 1). Because discrepancies exist among the ozone profiles derived from various methods, it would be useful to include a high resolution spectrometer on future ozone profile intercomparison experiments.

E. Journal Publications:

1. J. R. Gillis, A. Goldman, W. J. Williams, and D. G. Murcray: "Atmospheric Ozone Profiles from High Resolution UV Spectra Obtained with a Balloon-Borne Spectrometer." Applied Optics, 21, 413-420, February 1, 1982.

Material for January 1984 NASA Upper Atmosphere Report

A. Title of Research Task

Microwave Technology Development: Improving the Sensitivity of the Balloon Microwave Limb Sounder

B. Investigators and Institutions

Dr. P. Zimmermann (P.I.)
Dr. J. W. Waters
Dr. W. J. Wilson

C. Research Objectives

This task will improve, by a factor of at least 10, the sensitivity of the existing Balloon Microwave Limb Sounder (BMLS) by replacing its uncooled harmonic mixer with a cryogenically-cooled fundamental mixer and first-stage amplifier. The resulting system temperature will be below 1000K. These improvements are needed for:

(1) measuring diurnal variations in stratospheric $C\ell O$ profiles to test theoretical predictions

(2) ground-based measurements of longer-term variations in $C\ell O$ which have been observed by in situ resonance fluorescence techniques

(3) simultaneous comparison of BMLS and other $C\ell O$ measurements

The improvements will also substantially improve the BMLS measurements of O_3 and H_2O_2.

Also included in this task is the replacement of the existing BMLS filter banks and intermediate frequency electronics with duplicates of those systems for the MLS experiment on the UARS satellite. This will allow testing of the UARS measurements and data reduction algorithms.

D. Progress

All components for the cooled mixer and amplifier have been tested and are now being assembled into a system. The cooled system will be integrated in the existing BMLS and ready for a first flight in Spring 1984. The filter banks are being fabricated and will be integrated in the system after the Spring 1984 flight.

September 13, 1983

A. TITLE: ATMOS Array Processor

B. INVESTIGATORS:

Simmons, L. L., Farmer, C. B., Norton, R. H., Raper, O. F., Jet Propulsion Laboratory, Pasadena, CA.

C. ABSTRACT OF RESEARCH OBJECTIVES: The objective of this program is to upgrade the Atmospheric Trace Molecule Spectroscopy (ATMOS) Data Analysis Facility to insure sufficient throughput is available to handle, in the time available, the ATMOS data sets which will be acquired by the experiment from Spacelab 3 and subsequent flights. Additional capacity will be developed to maintain and dissiminate information from the accumulated data base while continuing to reduce and analyse data.

D. SUMMARY OF PROGRESS AND RESULTS: The ATMOS Data Analysis Facility configuration was reviewed and an ADPE acquisition plan (AP-490) was written and approved for the upgrade of the central processor and the array processor which are both to be used in the analysis of ATMOS data. The new configuration is intended to increase both the efficiency and the capacity of the facility. The changes being implemented as part of this task include upgrading the central processor, and acquiring additional terminals and hard copy equipment. Orders were placed for the needed equipment early enough to insure that costs would be incurred at the FY 83 GSA rates, which will result in a substantial savings in comparision to expected FY 84 GSA rates.

E. PUBLICATIONS: None

H. <u>CALIBRATION FACILITIES</u>

A. Calibration Facilities for NASA Payloads at SURF

B. Principal Investigator: Robert P. Madden
Center for Radiation Research
National Bureau of Standards

C. Research Objectives: The NBS spectrometer calibration beam line and its associated large spectrometer calibration chamber provide a common radiometric base for the wide range of scientific missions in the era of the space shuttle. Utilizing the calculable nature of synchrotron radiation from the National Bureau of Standards (NBS) Synchrotron Ultraviolet Radiation Facility (SURF II) and a well-characterized beam line, an accurate and long term stable radiometric base is maintained and made available to calibrate NASA payloads. This base covers the spectral region from 4 nm through the visible.

D. Summary of Progress and Results: The NBS spectrometer radiometric calibration beam line and its associated large spectrometer calibration chamber provide a common radiometric base for the wide range of scientific missions in the era of the space shuttle. During FY 83, a large number of calibrations of NASA related instruments were carried out at SURF. These calibrations are summarized in Table 1.

During FY 83 we have made several improvements to the calibration facilities:

- improved knowledge of SURF's orbital current to 1% by means of electron counting.
- constructed much improved orbital plane locator system and electronics.
- installed digital position readouts for horizontal and vertical motions at the 11.5 meter calibration position.
- obtained surveying equipment to improve and speed up alignment of beam line and users with the synchrotron radiation.
- improved pitch and yaw drive mechanisms for the gimbal inside the calibration chamber.
- made several improvements to the vacuum pumping systems.
- installed a redundant beam current monitoring system for improved reliability in knowledge of SURF's intensity.
- installed liquid N_2 system for cryobaffle which protects against contamination.
- constructed device to allow easy removal of entrance flange to calibration chamber.

Table I

FY 83 Spectrometer Calibrations

Institution	Investigator	Instrument	Number of times Calibrated (Projected to end of FY 83)
NRL	G. Carruthers	Stellar Spectrometer	2
NRL	G. Breuckner/ M. Van Hoosier	SUSIM	1
NASA/GSFC	J. Mentall/ D. Williams	Solar irradiance spectrometers	3
LASP	G. Mount/ R. Jakoubek	Solar irradiance spectrometers	2
Johns Hopkins University	P. Feldman/ S. Durance	Stellar Spectrometer	1

E. Journal Publications:

- VUV and XUV Radiometry Using Synchrotron Radiation at the National Bureau of Standards. E.B. Saloman, S.C. Ebner and L.R. Hughey, Optical Engineering 21, 951 (1982).
- Reduced Absolute Uncertainty in the Irradiance of SURF-II and Instrumentation for Measuring Linearity of X-Ray, XUV and UV Detectors. L.R. Hughey and A.R. Schaefer, Nucl. Inst. and Meth. 195, 367 (1982).
- Status Report: NBS/SURF Far UV Spectrometer Radiometric Calibration Facility. R.P. Madden, S.C. Ebner and L.R. Hughey, to be published in Middle Atmospheric Program Handbook.
- Status Report: NBS Far Ultraviolet Transfer Standard Detector Program. L.R. Canfield and R.P. Madden, to be published in Middle Atmospheric Program Handbook.
- Direct Determination of the Stored Electron Beam Current at the NBS Electron Storage Ring, SURF-II. A.R. Schaefer, L.R. Hughey and J.B. Fowler. Submitted to Metrologia.

553-G-84

Ozone Calibration Facility: Ultraviolet Photometer for Ozone Measurements and Calibrations

Arnold M. Bass
National Bureau of Standards

Abstract

An ultraviolet photometer of high accuracy and precision has been constructed for use as a primary standard in the calibration of ozone monitoring instruments. Calibration services have been provided to NASA and other agencies.

Summary of Progress and Results

Because of the need to provide a standard basis for comparison in instruments used in the monitoring of ozone concentrations in the atmosphere, a high-precision ultraviolet photometer was constructed at the National Bureau of Standards about six years ago. That instrument was a modified dual-beam photometer, three meters in length, that enabled us to characterize ozone concentrations with an uncertainty of about 2% over the range 50 ppb to 10 ppm. This facility was made available to the ozone-observing community and ozone calibrations were provided to NASA, EPA, various state agencies, and private industry.

Within the past two years we have completely redesigned the photometer and, with partial support from EPA, we have constructed a new standard instrument that is far superior to the original photometer. The new standard photometer utilizes a novel photometric system with an effective pathlength of about 1.6 meters. The precision of measurement now achieved is 0.2 ppb over the range 10 ppb to 1 ppm. The absolute accuracy of the measurement is limited to about 1.5% by the uncertainty in our knowledge of the ozone cross-section at 253.7 nm.

The new standard photometer is easily portable. It was used for pre-flight calibration of the ozone monitors that were flown in the NASA BOIC balloon program.

September 9, 1983

TASK SUMMARY

A. TITLE OF RESEARCH TASK- NASA High Speed Computing Facility

B. Investigators & Institutions-C. Bock and G. Mason/Goddard Space Flight Center

C. Abstract of Research Objectives
The purpose of this RTOP is to provide support for the procurement, operations, system programming, and user support activities for the NASA High Speed Computing Facility (NHSCF). The NHSCF provides a very high speed computational resource and related service to support mathematical modeling and other research activities in the applications and space sciences disciplines, including global weather, severe storms, climate, upper atmosphere, oceans, and geodynamics.

D. Summary of Progress & Results
During 1982-83, the High Speed Vector Processing System was installed and integrated and passed acceptance testing. Delivery of major system components occurred in June/July 1983. Integration and unit testing was conducted at Building 22 from July through September. Acceptance testing of the integrated system began October 12, and ended December 20, 1982.

Productive use of the CYBER 205 by GSFC investigators began during acceptance testing. The facility currently operates 3 shifts per week due to funding limitation. There are approximately 250 GSFC and outside users now using the facility.

Beginning in June 1983, block time assignments were allocated to each of the six major discipline areas using the NHSCF to ensure that each group would get its proper share of the 205 and so that job priorities within each discipline area could be managed by a designated discipline representative if desired.

Current NHSCF efforts are focused on solving technical problems, developing an accounting system, improving user support, developing documentation, and on increasing the staff to provide the computing support and services required by a growing user community.

The facility publishes a monthly NHSCF Newsletter and is currently preparing a Users Guide.

E. Journal Publications-N/A

II. LABORATORY STUDIES

A. KINETICS AND PHOTOCHEMISTRY

B. SPECTROSCOPY

A. KINETICS AND PHOTOCHEMISTRY

Yale University

Peter P. Wegener
APPLIED MECHANICS
Mason Laboratory
P.O. Box 2159
New Haven, Connecticut 06520
(203) 436-3563

September 1983

TO: Dr. R.E. Watson, Code EE-8, NASA Headquarters, Washington, DC 20546

FROM: P.P. Wegener

A. Title:

Experimental and Theoretical Study of Heteromolecular Nucleation of Vapors Occurring in the Atmosphere (NASA-Ames Agreement No. NAG-2-15)

B. Investigators and Institutions:

Peter P. Wegener, Franz Peters, Yale University
Philippe Mirabel, University of Strasbourg (Consultant)

C. Abstract:

Among the complex processes that may produce aerosols in the atmosphere, homogeneous, binary and heteromolecular nucleation may play a role, particularly in the stratosphere. A new experimental method to study the physical process of binary nucleation of H_2O and H_2SO_4 in an inert carrier gas at or near stratospheric states was devised. Preliminary experimental results show that the mentioned process is indeed a serious possibility and that numerical estimates of aerosols formed using the existing theory cannot be expected to be valid.

D. Summary to End of Grant 1982

A glass shock tube was developed in which binary nucleation of two supersaturated vapors in argon carrier gas could be studied at temperatures down to 185 K. Sample systems (e.g. ethanol-water) whose binary condensation is well known around room temperature were investigated for comparison with the existing theory of binary nucleation at low temperatures outside the range of known property data. Experimental results for these sample systems at low temperatures related to theory led to substantial discrepancies owing to uncertain extrapolations of vapor pressures, activities and surface tension of the binary liquid (or solid). In particular the application of bulk surface tension data — even if known — to small droplets causes errors due to radius effects causing concentration gradients near the drop surface and to possible dynamic effects. Since surface tension dominates the nucleation rate it was decided to rely on empirical results rather than on uncertain theory. The shock tube permits to reach stratospheric temperatures at supersaturated states. However, with the onset of nucleation determined by laser light scattering, it is difficult to detect faint clouds at low partial pressures of the condensates. This problem was solved and the work has provided nucleation studies at the lowest water vapor partical pressures ever observed. These experiments obtained at the proper temperatures still deal with vapor densities about one order of magnitude or larger above that found in nature. Yet water vapor *clearly condenses by nucleation* in the supersaturation state even at such low pressure. The systematic addition of trace amounts of H_2SO_4 vapor did not significantly affect the observed states of H_2O nucleation. In sum, experiments on H_2O/H_2SO_4 condensation by binary nucleation at stratospheric temperatures with the H_2O partial pressures higher than those found in nature, demonstrate that aerosols may be formed by this process. Comparison with theory is impractical owing to the lack of property data at these conditions. Further experimental work is urgently needed to extend the range of states in oder to settle the relative importance of this mechanism for aerosol formation.

E. Publications:

Franz Peters, "Homogeneous nucleation of ethanol and n-propanol in a shock tube". J. Chem. Phys. 77, 4788 (1982).

Franz Peters, "A new method to measure homogeneous nucleation rates in shock tubes". Experiments in Fluids 1. 143 (1983).

F. Peters, P.P. Wegener and R. Zahoransky, "Binary nucleation, new aspects of theory and experiment." To be submitted to J. Chem. Phys.

Peter P. Wegener

Task Title: Upper Atmosphere Research: Reaction Rate Measurements

Principle Investigator: L. J. Stief, Code 691, Goddard Space Flight Center

Co-Investigators: W. A. Payne, D. F. Nava, Code 691 and J. E. Allen, Jr., Code 963, Goddard Space Flight Center

Objectives:

The objectives of this research task are to measure absolute rate constants and reaction channel branching ratios for elementary reactions which may be important in the upper atmosphere and to develop and implement new techniques for the detection of transient atmospheric species. In order to achieve these goals, transient atmospheric species are produced via flash photolysis, laser photolysis, or microwave discharge and these species are detected and monitored by resonance flourescence, laser induced flourescence, intracavity absorption and mass spectrometry.

Summary of Progress and Results:

In the past two years, rate constants for nine reactions have been measured. Several of these rate constants have been measured as a function of temperature with an effort to make the measurements at temperatures characteristic of the stratosphere. Among the reactions for which temperature dependence studies have been completed is the reaction (1) $O + HBr \rightarrow OH + Br$. The rate constant, $k_1 = (6.73 \pm 1.93) \times 10^{-12} \exp(-1537 \pm 81/T)$ cm^3 $molecule^{-1}$ sec^{-1}, was determined by flash photolysis - resonance flourescence and indicates that reaction (1) is of minor importance in the regeneration of atomic bromine in the stratosphere.

In addition, at the request of the FAA, a temperature dependence study of the reaction (2) $NO + O_3 \rightarrow NO_2 + O_2$ was completed. Reaction (2) is important in odd oxygen destruction in the NO_x cycle. The rate constant k_2 was determined using a flow system and three independent detection techniques. The detection techniques included the monitoring of NO_2 chemiluminescence with excess NO and with excess O_3 and the monitoring of induced NO flourescence in the presence of excess O_3. The results of the three independent sets of data were found to agree within experimental error. The data showed curvature on an Arrhenius plot, however, over the temperature range $195 \leq T \leq 369$ K, the rate constant may be described by the expression $k_2 = (2.6 \pm 0.8) \times 10^{-12} \exp(-1435 \pm 64/T)$ cm^3 $molecule^{-1}$ sec^{-1}.

A temperature dependence study of the reaction (3) $Cl + H_2S \rightarrow HCl + HS$ has also been completed. The rate constant, $k_3 = (6.3 \pm 0.5) \times 10^{-11}$ cm^3 $molecule^{-1}$ sec^{-1} over the temperature 211K -353K was determined by flash photolysis resonance flourescence. This result is in agreement with the result $k_3 = (5.6 \pm 0.6) \times 10^{-11}$ obtained using the discharge flow-mass spectrometry technique at 298K. The latter measurement was made by L. J. Stief in the laboratory of the late Dr. M. A. A. Clyne at Queen Mary College, London. The results could indicate potential stratospheric significance for reaction (3) if, as has been suggested, volcanic eruptions inject sulfur compounds directly into the stratosphere.

The discharge flow-mas spectrometry technique was also used by L. J. Stief at QMC to determine the rate constants for the reactions (4) Cl + HS, (5) Cl + OCS, (6) ClO + NO and (7) ClO + NCl. The measurements were all at

298K and the results are $k_4 = 1.1 \times 10^{-10}$, $k_5 < 10^{-14}$, $k_6 = 1.9 \times 10^{-11}$ and $k_7 = 2.0 \times 10^{-11}$ cm^3 $molecule^{-1}$ sec^{-1}.

The technique of flash photolysis-resonance flourescence has been used to investigate the reaction (8) Cl + C_2H_2. Preliminary results at 298K indicate that reaction (8) is pressure dependent and $k_8 = 2.1 \times 10^{-12}$, 4.5×10^{-12} and 8.0×10^{-12} cm^3 $molecule^{-1}$ sec^{-1} at 10, 25, and 100 torr respectively. In addition, it appears from very recent experiments that the rate constant increases when the temperature is reduced to 210 K. Our room temperature study combined with a preliminary estimate that the reaction rate is 4 or 5 times faster at 210 K leads to the estimate that at 30 km in the stratosphere, the conversion of Cl to the stabilized radical C_2H_2Cl has a rate constant of approximately 10^{-11} cm^3 $molecule^{-1}$ sec^{-1} which is an order of magnitude faster than a previous estimate.

The final reaction studied was (9) N + NO_2. The experimental technique was discharge flow-resonance flourescence. Basic chemical complications (non-removable trace NO as reactant impurity and multi-reaction channels causing fast secondary reactions as well as inordinately high N atom sensitivity requirements) precluded high accuracy rate measurements. The room temperature rate constant $k_9 = (7.3 \pm 0.2) \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1} is probably too high. This study was the basis for a Master of Science degree by Z. U. Ndlela (Howard University, Washington, D. C.).

We are in the process of adding a collision free sampling mass spectrometric capability to our present discharge flow-resonance flourescence system. This will enable us to extend our kinetic measurements to include atom-radical and radical-radical reactions. Dr. John Brunning, NASA/NRC Resident Research Associate is assisting with the design and implementation of this capability. Work has also been initiated on the development of intercavity absorption as a sensitive technique for the detection and monitoring of atmospheric species.

Publications:

1. D. F. Nava, S. R. Bosco, and L. J. Stief, "Rate Constant for the Reaction of $O(^3P)$ with HBr from 221 to 455K", J. Chem. Phys. 78, 2443 (1983).
2. J. V. Michael, D. F. Nava, W. D. Brobst, R. P. Borkowski, and L. J. Stief, "Temperature Dependence of the Absolute Rate Constant for the Reaction of Hydroxyl Radicals with Hydrogen Sulfide", J. Phys. Chem., 86, 81 (1982).
3. J. V. Michael, J. E. Allen, Jr., and W. D. Brobst, "Temperature Dependence of the NO + O_3 Reaction Rate from 195 to 369K", J. Phys. Chem., 85, 4109 (1981).
4. Z. U. Ndlela, "Determination of the Rate Constant for N + NO_2 by the Technique of Discharge Flow Resonance Flourescence", M. S. thesis, Dept. of Physics aand Astronomy, Howard University, Washington, D.C. (1981).

CHEMICAL KINETICS OF THE UPPER ATMOSPHERE

W. B. DeMore
Jet Propulsion Laboratory
Pasadena, CA 91109

Objectives

This task is designed to elucidate the chemistry of the stratosphere by means of laboratory studies.

Reliable model calculations of the stratosphere require chemical rate coefficients and temperature dependences more accurate than presently available. This is especially true for the HO_x and ClO_x systems and their interactions with O_3. Also, there is an increasing need for pressure effects on reaction rates, along with more emphasis on the product distributions of many reactions where more than one product is possible.

Summary of Progress and Results

The following rate constant measurements and facility developments have been accomplished:*

1. $HO_2 + HO_2$, 298K, 1-3 torr, DF/MS-UV.
2. $HO_2 + HO_2$, $DO_2 + DO_2$, 240-417K, 50-1000 torr, 0-15 torr H_2O, theory, FP-UV.
3. $NO_2 + NO_3 + M$; T, P, FP/UV.
4. $O + HO_2$; 229-372K, DF/RF.
5. $k(O+HO_2)/k(O+OH)$; 299K, DF/RF.
6. $H + HO_2$; total k, OH branch, DF/RF.
7. "High pressure" flow system, HP-DF/RF.
10. $Cl + HNO_3$; 1-10 torr, 298-420K, DF/MS.
11. $Cl + NO_2 + M$; 1-10 torr, 264-417K, DF/MS.
12. UV White cell for DF/MS; DF/MS-UV.
13. $OH + HO_2$, DF/RF, 299K, 1 torr.
14. $HO_2 + NO_2$, FP/UV, T, P dependences.
15. $OH + SO_2$, DF/MS, T, P, M dependences.

8. OH + HCl; 2-50 torr, HP-DF/RF.

9. O + ClO; 1-3.5 torr, 236-422K, DF/MS.

16. OH + HNO_3, FP/RF, T, P, M dependences.

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* DF = discharge flow; MS = mass spectrometer; UV = ultraviolet spectrophotometry; FP = flash photolysis; RF = resonance fluorescence.

Publications

1. "Kinetics Studies of the HO_2 + HO_2 and DO_2 and DO_2 Reactions at 298K," S. P. Sander, M. Peterson, R. T. Watson, and R. Patrick, J. Phys. Chem. 86, 1236-1240 (19820.

2. "Kinetics of the Reaction O + HO_2 → OH + O_2 from 229 to 372K," L. F. Keyser, J. Phys. Chem. 86, 3439 (1982).

3. "Rate Constants for the Gas-Phase Reaction between Hydroxyl and Hydrogen Sulfide over the Temperature Range 228-518K," M. T. Leu and R. H. Smith, J. Phys. Chem. 86, 73 (1982).

4. "Rate Constant for the Reaction between OH and CS_2 at 298 and 520K," M. T. Leu and R. H. Smith, J. Phys. Chem. 86, 958 (1982).

5. "Temperature and Third-Body Dependence of the Rate Constant for the Reaction O + O_2 + M → O_3 + M," C. L. Lin and M. T. Leu, Internat. J. Chem. Kin. 14, 417 (1982).

6. "Rate Constants for the Reaction of OH with SO_2 at Low Pressure," M. T. Leu, J. Phys. Chem. 86, 4558 (1982).

7. "Kinetics of the Reaction of Hydroxyl Radicals with Nitric Acid," J. J. Margitan and R. T. Watson, J. Phys. Chem. 86, 3819-3824 (1982).

8. "Absolute Rate Constant of the Reaction OH + HO_2 → H_2O + O_2," L. F. Keyser, J. Phys. Chem. 85, p. 3667 (1981).

BIENNIAL REPORT

An Investigation of Several Reactions of Importance in Defining Stratopheric Halogen Chemistry

Principal Investigator: Dr. A. R. Ravishankara
Co-Investigators: Dr. P. H. Wine
Mr. J. M. Nicovich

Molecular Sciences Branch
Physical Sciences Division
Electromagnetics Laboratory
Engneering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia 30332

The main aim of this project is to better understand the chemistry of the stratosphere. We carried out laboratory measurements on stratospheric reactions. These measurements will help assess the potential impact of man-made emissions (such as chlorofluoro carbons and oxides of nitrogen) on the composition of the stratosphere. In addition to stratospheric reaction a few key tropospheric reactions which indirectly affect the stratosphere are also investigated. All the laboratory investigations involve measurement of rates of chemical reactions and when possible identification of the reaction products.

Our accomplishments to date are summarized below:

1. A laser based high pressure technique to measure the thermal rate coefficients of reactions between two free radicals was developed. The reaction of $O(^3P)$ with HO_2 was investigated at 7 pressures of N_2 ranging from 10 to 500 torr N_2. The measured value of the rate coefficient is $(6.2 \pm 1.1) x 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, independent of pressure. A few measurements on the reaction of $O(^3P)$ with OH were also carried out.

2. The kinetics of the reactions $O(^3P)$ with H_2O_2 (k_2) and O_3 (k_3) were measured as functions of temperature. The measured rate coefficients are: $k_2 = (1.13 \pm 0.54) x\ 10^{-12} \exp[-(2000 \pm 160)T]$ and $k_3 = (5.6 + \ 2.1) x\ 10^{-12} \exp[-(1950 \pm 110)/T]$ (units are cm^3 $molecule^{-1}$ s^{-1}, all errors are 2σ).

3. The rate coefficient for a reaction of OH with CO was measured as functions of pressure, identity of diluent gas, temperature, and added O_2 concentration. SF_6 was observed to increase the measured rate coefficient as a function of its pressure. O_2 was found to have no effect. The yield of H atom was found to be unity in Argon.

4. The studies of the reactions of $Cl(^2P)$ with a series of partially chlorinated ethanes (CH_3CCl_3, CH_3CH_2Cl,CH_3CHCl_2, CH_2ClCH_2Cl, $CH_2ClCHCl_2$) were completed. The rate coefficients were measured as functions of temperature.

5. The studies of the reactions of $O(^1D_2)$ with various stratospheric molecules (H_2O, CH_4, H_2, N_2, and CF_2O) were completed.

Publications

1. "Pulsed Photolysis Study of the Reaction Between $O(^3P)$ and HO_2", A. R. Ravishankara, P. H. Wine, and J. M. Nicovich, J. Chem. Phys., 78, 6629(1983).

2. "Kinetics of $O(^3P)$ Reactions With O_3 and H_2O_2," P. H. Wine, J. M. Nicovich, R. J. Thompson, and A. R. Ravishankara, J. Phys. Chem., 87, xxx, 1983.

3. "Reactive and Non-Reactive Quenching of $O(^1D_2)$ by COF_2", P. H. Wine and A. R. Ravishankara, Chem. Phys. Lett., 96, 129 (1983).

4. "An Upper Limit for the Rate of the Reaction of $Cl(^2P_J)$ with Methyl Chloroform",P. H. Wine, D. H. Semmes, and A. R. Ravishankara, Chem. Physics Letts., 90, 128 (1982).

5. "O_3 Photolysis at 248 nm and $O(^1D_2)$ Quenching by H_2O, CH_4, H_2O, and N_2O; $O(^3P_J)$ Yields", P. H. Wine and A. R. Ravishankara, Chemical Physics, 69, 365 (1982).

6. "Kinetics Study of the Reaction of OH With CO From 250 to 1040K", A. R. Ravishankaka and R. L. Thompson, Chemical Physics Letts.,xxx,xxx, 1983.

7. "Kinetics of $Cl(^2P_J)$ Reactions With Chloroethanes CH_3CHCl_2, CH_2ClCH_2Cl, and $CH_2ClCHCl_2$", P. H. Wine and D. H. Semmes, J. Phys. Chem., 87, xxx, 1983.

HOMOGENEOUS AND HETEROGENEOUS PROCESSES OF ATMOSPHERIC INTEREST

Investigators:

David M. Golden, John R. Barker, Michel J. Rossi,
Paula L. Trevor, and Roger Patrick

All at the Department of Chemical Kinetics
SRI International, Menlo Park, CA 94025

RESEARCH OBJECTIVES

The research was undertaken in a continuing effort to understand the chemistry of the terrestrial atmosphere. Both heterogeneous and homogeneous processes can be important and processes of both types were investigated. The three tasks undertaken were (1) investigation of the wavelength-dependent photolysis and product formation of chlorine nitrate ($ClONO_2$), pernitric acid ($HOONO_2$), and dinitrogen pentoxide (N_2O_5), (2) continue to critically evaluate atmospheric chemical reaction rate data within the scope of thermochemical kinetics, and (3) use low-pressure flow techniques to investigate heterogeneous chemical processes on sulfuric acid surfaces.

SUMMARY OF PROGRESS AND RESULTS

Task 1: Very Low-Pressure Photolysis Studies.

Although not complete, our research shows that the primary photolysis products of $ClONO_2$ photolysis are Cl-atoms and NO_3 free radicals; O-atoms are not an important product. Our result is in agreement with our earlier work. Photolysis of N_2O_5 has also been investigated to determine whether O-atoms are found, as has been claimed. The results show that O-atoms are, at most, a minor or secondary photolysis poroduct, and the primary products appear to be NO_2 and NO_3.

Task 2: Critical Evaluation of Kinetics Data

D. M. Golden has continued to participate as a member of the NASA Data Evaluation Panel. As a result of this work, a comprehensive evaluation of the low-pressure limiting three-body reactions has been completed.

In a separate effort, a theoretical study of HO_2 radical self-reaction has been completed that raises more questions about the dynamics of this interesting process.

Ion-molecule reactions have also been investigated in conjunction with John I. Brauman and James Dodd of the Stanford University Chemistry Department. This work shows that the locked-rotor tansition states are not appropriate as rate-controlling free energy maxima in ion-molecule interactions.

Task 3: Heterogeneous Processes on Sulfuric Acid Surface

From earlier studies in this laboratory, it was established that dry N_2O_5 is lost on sulfuric acid surfaces with a per-collision probability of $\gamma \sim 4 \times 10^{-5}$. The effect of humidity was investigated in the present work to determine whether N_2O_5 losses are increased to the point of becoming important to atmospheric chemistry. The results showed that γ is larger than our earlier studies indicated $(\gamma \approx 3 \times 1^{-4})$, but it does not vary significantly as water vapor is introduced. This new value for γ results in an estimate for heterogeneous loss of N_2O_5 that is about one order of magnitude less important than unimolecular reaction of N_2O_5 at 20 km.

Journal Publications (1982-1983)

"A Computational Study of the $HO_2 + HO_2$ amd $DO_2 + DO_2$ Reactions," by Roger Patrick, John R. Barker, and David M. Golden. J. Phys. Chem., in press.

"Three-Body Reactions," Roger Patrick and David M. Golden, Int. J. Chem. Kinetics, in press.

"Very Low-Pressure Photolysis of t-Butyl Nitrite at 240 nm," by Paula L. Trevor and David M. Golden, J. Photochem., in press.

Photochemical and Kinetic Measurements of Atmospheric Constituents vis-a-vis Their Role in Controlling Stratospheric Ozone

Principal Investigator: Dr. Michael J. Kurylo

Co-Investigator: Dr. Allan H. Laufer

Center for Chemical Physics
National Bureau of Standards
Washington, DC 20234

Research Objectives: This task focusses on the elucidation of stratospheric photochemical kinetics through laboratory studies of select chemical reaction systems. While these studies are designed to answer questions regarding possible catalytic destruction of O_3 associated with the release of chlorine containing compounds to the atmosphere, they are part of a more generic program designed to examine the interrelation of the various chemical cycles in both the stratosphere and troposphere.

Progress and Results (1982-83):

1) The kinetics of the reaction of OH radicals with H_2O_2 was studied by the flash photolysis resonance fluorescence (FPRF) technique over the temperature range 250-370 K. The present results together with those of three other recent studies have been used to derive the expression

$$k = (2.9 \pm 0.3) \times 10^{-12} \exp[(-160 \pm 30)/T] \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}$$

consistent with that now recommended for stratospheric modeling.

An elaborate computer simulation of this reaction system reveals significant chemical complexities in the pre-1980 studies.

2) The reaction of Cl atoms with nitric acid was studied by FPRF at temperatures, between 243 and 298 K. The results are consistent with the Arrhenius expression

$$k = 5.1 \times 10^{-12} \exp(-1700/T) \ cm^3 molec^{-1} s^{-1}$$

although rather large error limits on the individual rate constants are required to account for uncertainties due to potential NO_2 impurities. Nevertheless, the reaction is unimportant as a stratospheric Cl loss process.

3) A reinvestigation of the Cl + $ClONO_2$ reaction by FPRF from 220-296 K indicates an error in our earlier (1977) measurements probably due to O atom resonance fluorescence interference. The derived Arrhenius expression

$$k = 7.3 \times 10^{-12} \exp(165/T) \ cm^3 molec^{-1} s^{-1}$$

is in good agreement with another recent study and accounts for discrepencies in reported primary quantum yields for $ClONO_2$ photolysis.

4) The FPRF technique was used to monitor the kinetics of the reaction of OH and Cl with CH_3CN. The OH data from 250-363 K can be fit to the equation

$$k = 6.2 \times 10^{-13} \exp(-1030/T) \ cm^3 molec^{-1} s^{-1}$$

An upper limit at 298 K of 2.0×10^{-15} $cm^3 molec^{-1} s^{-1}$ can be set for the Cl atom reaction.

5) A flash photolysis kinetic absorption spectroscopy apparatus has been constructed and is being used to investigate HO_2 kinetics. Initial experiments have yielded rate constant measurements for $HO_2 + HO_2$ in the presence of O_2 in good agreement with other recent studies.

Journal Publications (1982-83)

1. M. J. Kurylo, K. D. Cornett, and J. L. Murphy, "The Temperature Dependence of the Rate Constant for the Reaction of Hydroxyl Radicals with Nitric Acid", J. Geophys. Res., 87, 3081 (1982).
2. M. J. Kurylo, J. L. Murphy, G. S. Haller, and K. D. Cornett, "A Flash Photolysis Resonance Fluorescence Investigations of The Reaction $OH + H_2O_2 \rightarrow HO_2 + H_2O$", Int. J. Chem. Kinetics, 14, 1149 (1982).
3. M. J. Kurylo, J. L. Murphy, and G. L. Knable, "Rate Constant Measurements for the Reaction of Cl Atoms with Nitric Acid Over the Temperature Range 240-300 K", Chem. Phys. Letters, 94, 281 (1983).
4. M. J. Kurylo, G. L. Knable, and J. L. Murphy, "A Reinvestigation of the $Cl + ClONO_2$ Reaction by Flash Photolysis Resonance Fluorescence", Chem. Phys. Letters 95, 9 (1983).

A. HIGH RESOLUTION FOURIER TRANSFORM INFRARED SPECTROMETER FOR KINETIC STUDIES

B. Carleton J. Howard
NOAA, ERL, AL
325 Broadway
Boulder, CO 80303

C. The objectives of this program are to obtain and to put into operation a high resolution Fourier transform interferometer. The FTS will be used to take spectra of stable and transient atmospheric molecules. These data are used to identify and quantify critical species in atmospheric field studies. The project also seeks to develop kinetic data on the products and intermediates of important atmospheric reactions. These data are required for models that simulate the enivronmental effects of natural and man-made chemicals.

D. The FTS was installed in May 1983. A small multipass absorption cell was obtained to test the high resolution performance of the instrument in the IR region. The absorption spectrum of NO was recorded near 5μm wavelength at high resolution. This demonstrated that the instrument performance was within a factor of two of the resolution specification $\Delta\nu = 0.002\ cm^{-1}$. After the manufacturer's representatives left several problems surfaced with the operation of the FTS, two of these problems practically halted work on the system! (1) frequent misalignment of the mirrors during scans and (2) detector problems. The detector problem was corrected and the misalignment problem will be remedied soon when the manufacturer replaces the moving mirror assembly with a redesigned system.

A long path absorption cell has been connected to the FTS for testing its performance in the visible and near UV wavelength regions. Spectra of gases such as O_3, NO_2, NO_3, Br_2 and I_2 will be recorded. A long path cell that will be dedicated to the FTS system is under construction. This cell will allow spectra to be taken with an evacuated optical path and at various gas temperatures. One important project that will be pursued is a search for molecules that are stable only at low temperatures.

SUMMARY OF 1982-83 RESEARCH

A. The Sources of Stratospheric NO and N_2O

B. SRI International:

G. Black
R. M. Hill
R. L. Sharpless
T. G. Slanger

San Jose State University:

N. Albert

C. The research objectives have been to learn about stratospheric sources and sinks of N_2O and NO beyond those included in current models. In the most basic sense, it is a question of evaluating the effect of electronic energy in the N_2-O_2system, i.e. can it be substantiated that either N_2^* + O_2 or O_2^* + N_2 contribute to stratoshperic production of N_2O (or NO)? Specifically, the reaction efficiency of $N_2(A) + O_2 \longrightarrow N_2O + O(^3P)$ has been studied, as well as the stability of N_2O in an O_3-N_2O-N_2 system subjected to 2537 Å uv photolysis.

D. Investigations by two groups on the efficiency of $N_2(A^3\Sigma_u^+)$ quenching by O_2 to produce N_2O had led to contradictory results. Zipf had reported this reaction to be 60% efficient, and therefore an important source of stratospheric N_2O, whereas Iannuzzi and Kaufman had concluded that the N_2O yield was only 2%, and therefore stratospherically unimportant. It was clearly essential to determine which of these conclusions is correct.

We carried out the experiment with a well-characterized $N_2(A^3\Sigma_u^+)$ source, an electron-beam pumped N_2-Ar discharge. By adding O_2 to this system, we were able to determine how efficiently N_2O was produced, and after having established that N_2O itself was not destroyed under the experimental conditions, we were able to show that the upper limit for the N_2O quantum yield was 8%. As there are conceivably other N_2O sources in the experiment, it is clear that our results strongly support those of Iannuzzi and Kaufman, and not those of Zipf.

In attempting to investigate O_2^*-N_2 chemistry as an N_2O source, we found evidence for N_2O destruction under conditions where it is expected to be stable. As this observation interfered with our attempts to monitor N_2O production, it was evident that we needed to investigate this process first.

What was noted was that 2537Å photodissociation of an O_3-O_2-N_2O mixture in an N_2 buffer led to N_2O disappearance, in spite of the fact that N_2O does not absorb radiation at this wavelength. Furthermore, the $O(^1D)$ produced by O_3 photodissociation, which can react with N_2O, is quenched by the excess N_2, so it is not at all obvious how N_2O is destroyed. In fact, both O_3 and uv photons are needed for the process.

In investigating the OH(A) - N_2 system as an N_2O source, Zipf has also found an N_2O destruction process that appears to be associated with the presence of O_2. It seems reasonable to assume that the chemistry responsible for the N_2O destruction is the same in both systems, and our present year's work is devoted to achieving an understanding of how the N_2O disappears, as this may be not only a laboratory problem, but a process taking place in the stratosphere.

E. Journal Publications

"Laboratory Studies on N_2O Relevant to Stratospheric Proceses" by G. Black, R.M. Hill, R.L. Sharpless, T.G. Slanger, and N. Albert., J. Photochem. 22, 369 (1983).

A. Title of Research Task

Biogenic Origin of Methyl Chloride in The Atmosphere and Oceans.

B. Investigators and Institutions

Minoo N. Dastoor, Yuk Y. Yung, Steven L. Manley & Wheeler J. North
California Institute of Technology
Pasadena, California

C. Abstract of Research Objectives

The role of the biota in the maintenance and modulation of the major constituents of the atmosphere (i.e., N_2, O_2, CO_2) is well established. In contrast, the biotic interactions involving trace atmospheric constituents are unknown. Of particular importance, is the atmospheric ozone layer. The objective of this research endeavor is to perform a study to evaluate the contribution of certain marine algae (i.e., Macrocystis pyrifera) which evidence suggests should be involved in the production of methyl halides, specifically methyl chloride. Marine macroalgae may produce methyl chloride by direct biosynthesis, by producing an intermediate compound which is chemically or microbially converted to methyl chloride in seawater or by supplying, after death, certain metabolites for microbial degradation. An understanding of the natural production of methyl chloride is required to construct a suitable atmospheric halogen budget and to determine its contribution to atmospheric ozone destruction. We propose to identify the marine algae species which are responsible for methyl halide production. If an indirect mechanism of methyl halide production is required, then we will investigate the possibility that non-photosynthetic and/or methanogenic bacteria may utilize certain marine algae to produce methyl halides. The production of methyl halides will be quantified and a correct atmospheric halogen budget based on the results will be constructed. Our approach will employ laboratory culturing of marine algae and methanogenic bacteria, and quantitative chemical analysis. Quantitative field measurements of marine kelp bed (Point Loma, CA) known to have elevated levels of methyl chloride will also be conducted. This research project is a joint JPL/Campus collaborative effort.

D. Summary of Progress and Results

1) Electron capture-gas chromatography methods and conditions were established for the detection of methyl chloride, methyl bromide and methyl iodide at parts per trillion level.

2) Sampling methods and laboratory culturing techniques for macrocystis tissue samples were successfully accomplished.

3) Qualitative data from preliminary experiments with macrocystis indicated:

   a. Senescent laminal tissue produces more methyl halides than either immature or mature tissue types.

b. Autoclaved tissue innoculated with marine bacteria shows methyl halide production. Non-innoculated autoclaved tissue shows no production. Hence, suggesting bacterial intervention for the halide synthesis.

c. Kinetic studies of dissolved oxygen concentration and bacterial growth indicate methyl halide production could be caused by anaerobic bacteria.

d. *M. pyrifera* is not the primary source of methyl halides (i.e., direct biosynthesis), but a suitable substrate for subsequent microbial growth and formation of methyl halides.

E. Journal Publications

A manuscript in preparation for submission to Science.

A. Laboratory Studies of the Kinetics of Tropospheric and Stratospheric Atom and Radical Reactions

B. Principal Investigator: Frederick Kaufman, University Professor of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260

C. Abstract of Research Objectives: The research objectives are three-fold: (a) to provide direct measurements of elementary rate parameters for important atom/radical reactions needed in the modeling of the troposphere or stratosphere; (b) to compare experimental data with theoretical prediction at various levels of sophistication in order to test and expand the predictive power of theory; and (c) to improve radical concentration measurement techniques in the laboratory, both to facilitate the necessary reaction rate studies and to lay the groundwork for future application in field measurements.

D. Summary of Progress and Results

Excellent progress was achieved. In laboratory rate measurements, two major classes of reactions were studied: (i) simple, "direct," H-atom abstraction by OH where there exists an energy barrier and a well-defined transition state; and (ii) non-simple, "complex" processes that proceed via a bound intermediate whose well depth, entrance and exit channels, and ergodic or non-ergodic behavior greatly complicate the interpretation of the limited, available data.

The "direct" H-abstraction steps were of the $OH + RH \rightarrow H_2O + R$ type where the RH's were CH_4 and all nine Cl- and F-substituted methanes[1,2] having at least one abstractable H-atom, and, in a recent paper, C_2H_6 and four Cl- and F-substituted ethanes.[3] Most of these reactions are of direct atmospheric interest as tropospheric interception reactions of halocarbons, thus controlling the atmospheric lifetime of the particular RH, or as regulators of the stratospheric altitude concentration profiles of naturally occurring minor species such as CH_4, C_2H_6, or CH_3Cl. Using this large data base over a wide temperature range, we were able to make a major assessment of the predictive power of semi-empirical, Benson-Golden thermochemical transition state theory, at least in terms of the calculated pre-exponential A-values of the reactions. The principal results: good agreement between experiment and theory on average for a <u>non-linear</u> $O\text{-}H\diagup^{C}$ approach in the abstraction, but a general inability to predict A-values or substituent effects to within better than a factor of two.

The "complex" reactions included O + HO_2,[4] H + HO_2[4] (with its three product channels), OH + HO_2,[5] and O + C_2H_4.[6] The rate constants of the three HO_2 reactions were found to be very large, indeed, inconsistent with simple H-abstraction. This is particularly clear for H + HO_2 whose major product channel (89%) is OH + OH, indicating the intermediate formation of vibrationally highly excited $H_2O_2^{\dagger}$ which quickly decomposes to OH + OH. The relatively small contribution (∿9%) of the H_2 + O_2 product channel is in good agreement with modeling calculations of the upper stratosphere and mesosphere. For the O + C_2H_4 reaction, our finding of ∿80% direct H-atom yield supports recent molecular beam results, but leaves unanswered several questions regarding intermediates as well as the CHO + CH_3 product channel.

Our work on the temperature dependence of the important OH + HO_2 reaction is nearly complete, indicating a fairly strong, negative temperature dependence and will be submitted for publication very soon. A general, brief review of progress and prospects in elementary reaction kinetics/dynamics of polyatomics[7] was presented and published as part of the celebration of the 50th anniversary of Eyring and Polanyi's famous paper "On Simple Gas Reactions." It raises critical points of the (lack of) interaction between experiment and theory for small polyatomic systems.

E. Journal Publications

1. "Kinetics of the Reaction of Hydroxyl Radicals with CH_4 and with Nine Cl- and F-substituted Methanes. I. Experimental Results, Comparisons, and Applications," K-M. Jeong and F. Kaufman, J. Phys. Chem. 86, 1808 (1982).
2. "Kinetics of the Reaction of Hydroxyl Radicals with CH_4 and with Nine Cl- and F-substituted Methanes. II. A Test of Transition State Theory," K-M. Jeong and F. Kaufman, J. Phys. Chem. 86, 1816 (1982).
3. "Kinetics of the Reactions of OH with C_2H_6, CH_3CCl_3, $CH_2ClCHCl_2$, $CH_2ClCClF_2$, and CH_2FCF_3," K-M. Jeong, K-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem., in press.
4. "Kinetics and Product Channels of the Reactions of HO_2 with O- and H-atoms at 296 K," U. C. Sridharan, L. X. Qiu, and F. Kaufman, J. Phys. Chem. 86, 4569 (1982).
5. "Temperature Dependence of the OH + HO_2 Reaction," U. C. Sridharan, L. X. Qiu, and F. Kaufman, to be submitted to J. Phys. Chem.
6. "Primary Products of the O + C_2H_4 Reaction," U. C. Sridharan and F. Kaufman, Chem. Phys. Letters, in press.
7. "Progress and Prospect in Elementary Reaction Kinetics/Dynamics of Polyatomics," F. Kaufman, Berichte Bunsenges. Physik. Chem. 86, 362 (1982).

MATRIX-ISOLATION-INFRARED SPECTROSCOPIC STUDIES
OF
CHLORINE NITRATE ISOMERS

Principal Investigators: John H. Hall, Jr.
Subhash C. Bhatia

Institutions: Atlanta University Center Science Research Institute
Georgia Institute of Technology

Abstract of Research Objectives

The structure of chlorine nitrate isomers was investigated using matrix-isolation-infrared spectroscopy and Hartree-Fock-Self-Consistent-Field (HFSCF) studies. The objective was to determine whether the molecule exists in different isomeric forms, and if so, to determine the respective structures.

Summary of Progress and Results

The matrix-isolated-infrared spectra of chlorine nitrate produced from the reaction $ClO + NO_2\ (+M) \longrightarrow ClNO_3\ (+M)$, and the bulk synthesis show absorptions due to $ClONO_2$ (C_{1h} structure) and ClOONO (Table 1).

Table 1: Observed Molecular Vibrational Frequencies (cm^{-1}) for $ClONO_2$ and ClOONO in Matrix-Isolated Chlorine Nitrate ($ClNO_3$/Ar, 1:1000)

Vibrational Mode	$ClONO_2$	ClOONO
N=O	1726.9	1717.6
Unassigned		1431.9
NO_2 asy stretch	1287.6	
NO' stretch	556.6	896.9
O-O stretch		855.0
O-Cl stretch	807.7	428.2 or 412.0
NO_2 scis	781.3	
NO_2 wag	712.5	
Unassigned		705.0
O-N-O' bend		556.3
O-O-N bend		445.6
NO_2 rock	428.2	

Isotopic substitution experiments with $Cl^{18}O$ and $N^{16}O_2$ show absorption consistent with the production of $Cl^{18}O - {}^{16}ON^{16}O$ at $840 cm^{-1}$ ($^{18}O - {}^{16}O$ stretch). Ab-initio HFSCF calculations at the 4-31G and near Hartree-Fock (polarized double zeta, PDZ) levels provide further evidence for the existence of ClOONO isomers. The $ClONO_2$ (C_{1h} structure) is only 16 kcal/mole higher in energy than ClOONO. It should be noted that isomers differing in energy by as much as 50 kcal/mole have been trapped from the gas-phase and spectroscopically characterized in inert matrices at 10K. The $OClNO_2$ isomer of chlorine nitrate is calculated to be 49 kcal/mole higher in energy than the C_{1h} structure, while the ONOClO isomer is computationally unstable (Table 2). The geometry of each isomer was optimized at the 4-31G level. The planar structure for $ClONO_2$ is favored over the non-planar structure by 80 kcal/mole.

Table 2. Energy Analysis for Chlorine Nitrate

	4-31G	PDZ[a,b]
$ClONO_2$	-737.3171	-738.2071
ClOONO	-737.2910	-738.1814
$OClNO_2$	-737.2079	-738.1284

[a]Calculations were performed using the GAUSSIAN 80 SCF package. The PDZ basis-set employed an (11s7p) basis on chlorine contracted to (6s4p) and a (9s5p) basis on ozygen and nitrogen, contracted to (5s3p). A single d orbital (exponent = 0.55) was also placed on chlorine.

[b]Energies are in atomic units (a.u.); 1 a.u. = 625 kcal/mole.

Unrestricted Hartree-Fock (UHF) calculations were performed on the lowest triplet states of $ClONO_2$ and ClOONO. The triplet state was found to be unstable, with $ClONO_2$ dissociating into Cl + NO_3, and ClOONO dissociating into ClOO + NO.

Publications

1. S. C. Bhatia, M. George-Taylor, C. W. Merideth and J. H. Hall, Jr., Low-Temperature Infrared Spectrum of Chlorine Nitrate and Evidence for the Existence of ClOONO. J. Phys. Chem., 1983, 87, 1091.

2. S. C. Bhatia and J. H. Hall, Jr., Ab-Initio Self-Consistent-Field Studies of $ClNO_x$ ($x = 1, 2, 3$), submitted for publication, J. Chem. Phys.

SUMMARY FOR NASA RESEARCH GRANT 825-UA-269

A. "Ultraviolet Photolysis of Ions of Stratospheric Importance"
CONTRACT STARTING DATE: June 1, 1983

B. Principal Investigator: Prof. F. Sherwood Rowland
Institution: Department of Chemistry
University of California
Irvine, California 92717

C. Research Objectives: Measurement of the photon absorption coefficients for various ions of stratospheric importance. The ultraviolet radiation intensity in the upper and middle stratosphere is extremely intense, and most complex molecular species have sufficiently strong photochemical interaction that their atmospheric lifetimes are very short (often only of minutes) in the 30-50 km altitude range. Careful measurement of ion concentrations in the atmosphere and reaction rates in the laboratory offer the potential for inference of neutral species concentrations from measured ion intensities. Current mechanistic interpretations of such reactions rely on the assumption that these complex ions survive long enough to be terminated by ion/ion reaction with an ion of opposite charge even in the ultraviolet radiation field, a time of approximately 10,000 seconds. The photon absorption coefficients of these ions [e.g. $Na(H_2O)_3^+$] are to be measured in the 193-308 nm wavelength region with an instrument composed of an excimer laser plus an ion cyclotron resonance cell for ion detection.

D. Summary of Progress and Results for the period June 1-Aug.15, 1983

A special cooled ion-source has been built for the ion cyclotron resonance apparatus in order to favor higher concentrations of cluster ions involving H_2O, such as the polyatomic H_2O species $Na(H_2O)_3^+$ and $K(H_2O)_3^+$. Testing of the ion yields from this ion source are now just beginning. The excimer laser has been ordered, with delivery scheduled for late August.

E. Journal Publications: none

A. Title of Research Task:

Gas Phase Reactions of Compounds of Interest for Stratospheric Chemistry.

B. Principal Investigator: Mario J. Molina.

Co-investigators: Luisa T. Molina; John Lamb; Craig Smith.

Institution:

University of California, Department of Chemistry, Irvine, California 92717.

C. Research Objectives:

To provide laboratory data on chemical and photochemical reactions which play a significant role in the stratosphere. Ultraviolet absorption cross sections are measured in order to predict atmospheric photodissociation rates. Rate constants for elementary reaction steps are measured primarily using flash photolysis coupled with time-resolved detection of transient species and FTIR characterization of reactants.

D. Summary of Progress:

The photochemical behavior of several brominated fluorocarbons has been investigated. The gas-phase photolysis of CBr_2F_2 was studied in the presence of 1 atm of air at 206, 248, and 302 nm. The only products formed are CF_2O and Br_2, and within experimental error the measured quantum yields for the disappearance of CBr_2F_2 and for the appearance of CF_2O and Br_2 are unity. These results are in disagreement with earlier literature reports suggesting significantly smaller quantum yields and indicating that 265-nm radiation produces excited CBr_2F_2 molecules long lived enough to permit collisional stabilization.

The absolute rate constants for the reactions of $OH + HO_2NO_2$ (1) and $OH + HNO_3$ (2) have been measured with the technique of flash photolysis resonance fluorescence over the temperature range 240 to 330 K at 760 torr He for reaction (1) and from 240 to 370 K at 50 and 760 torr He for reaction (2). Reactant concentrations were monitored continuously by ultraviolet and infrared spectrophotometry. The data can be fitted to the following Arrhenius expressions:

$$k_1 = (5.9 \pm 0.4) \times 10^{-13} \exp [(650 \pm 30)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_2 = (8.3 \pm 0.9) \times 10^{-15} \exp [(850 \pm 40)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

The absolute rate constant for the OH + HCl reaction was measured in a similar apparatus, using both laser and conventional flash photolysis. The results yield essentially the same activation energy as the literature value, but the absolute rate obtained was about 20% larger.

E. Journal Publications (1982-1983):

Quantum Yields for Photodissociation of CBr_2F_2 in the 200-300 nm Region. Journal of Physical Chemistry, 87, 1306 (1983).
L. T. Molina and M. J. Molina.

Kinetics of the Reaction of OH with Pernitric and with Nitric Acids. International Journal of Chemical Kinetics, in press, 1983.
C. A. Smith, L. T. Molina, J. J. Lamb, and M. J. Molina.

PHOTOCHEMISTRY OF THE UPPER ATMOSPHERE

W. B. DeMore
Jet Propulsion Laboratory
Pasadena, CA 91109

Objectives

This task is intended to elucidate the photochemistry of the stratosphere by means of laboratory studies. The concentrations of several stratospheric trace species are limited by the rates of photolysis, which in turn are related to the absorption cross sections. Laboratory measurements are required for some important species for which cross section data, product distributions, and quantum yields are not known with sufficient reliability. An additional need for cross section data arises in connection with kinetic studies, owing to the fact that absorption photometry is frequently used for concentration measurements. Field measurement programs based on UV absorption also require this data.

Summary of Progress and Results

A number of photolysis quantum yields, product yields, and rate constants for atmospheric processes have been determined. For chlorine nitrate photolysis, the quantum yields of atomic chlorine and atomic oxygen were measured at 266 and 355 nm at 298 and 238K. The rate constant for the reaction $Cl + ClONO_2 \rightarrow Cl_2 + NO_3$ was measured, showing that the reaction is much faster than previously believed. This observation cleared up several puzzling problems in the literature, and further showed that this reaction is a good source of NO_3 for additional kinetics studies. It was also shown that the reaction $ClO + NO_2$ produces only $ClONO_2$, and not isomers of that product, as had been suggested in other studies. The rate constant for the reaction of HO_2 with $ClONO_2$ was shown to be less than 6 x $10^{-15} cm^3/s$, thus proving that it is unimportant in the stratosphere.

The rate constant for the OH + CO reaction was studied, with particular emphasis on the pressure and oxygen dependence. The results showed that, contrary to previous reports, there is an enhancement of the rate constant upon pressurization with O_2-free N_2, and that O_2 has no effect on the reaction rate other than as a pressurizing gas.

An apparatus has been constructed for the study of reaction intermediates and products, utilizing a Bomem Model DA-002 Fourier Transform Infrared Spectrometer coupled to both a static photolysis White cell and a flow-discharge apparatus.

Publications

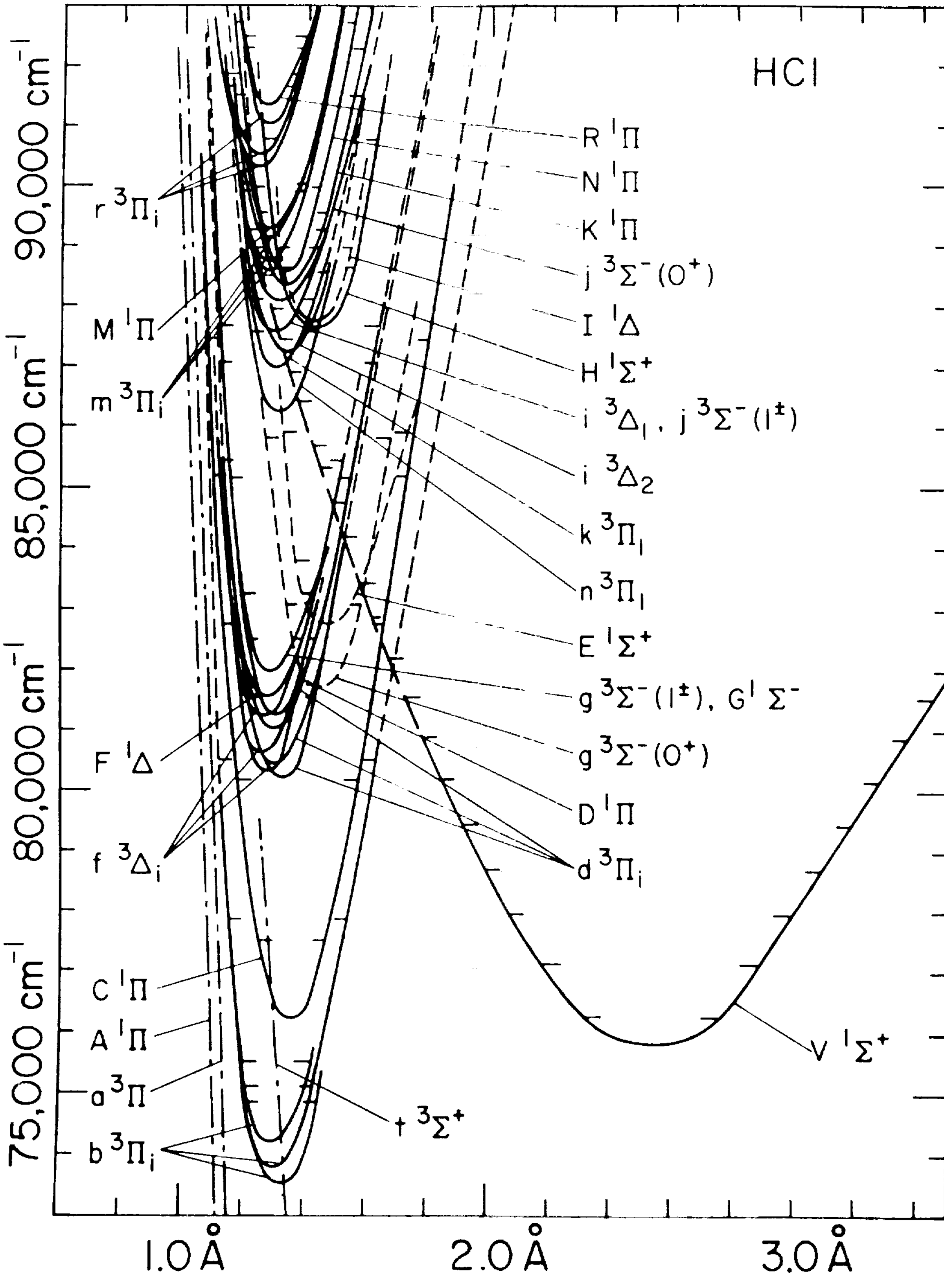
1. "Catalytic Processes in the Atmospheres of Earth and Venus," W. B. DeMore and Y. L. Yung, Science 217, pp. 1209-1213 (1982).
2. "Chlorine Nitrate Photochemistry: Photolysis Products and Kinetics of the Reaction Cl + $ClONO_2 \rightarrow Cl_2 + NO_3$," J. J. Margitan, J. Phys. Chem. 87, pp. 674-679 (1983).
3. "Clorine Nitrate: The Sole Product of the ClO + NO_2 + M Recombination," J. J. Margitan, J. Geophys. Res. 88, pp. 5416-5420 (1983).
4. "Rate Constant and Possible Pressure Dependence of the Reaction OH + HO_2," W. B. DeMore, J. Phys. Chem. 86, p. 121 (1982).
5. "Kinetics of the Reaction of Hydroxyl Radicals with Nitric Acid," J. J. Margitan and R. T. Watson, J. Phys. Chem. 86, p. 3819 (1982).

A. SPECTRAL STUDIES RELATED TO DISSOCIATION OF HBr, HCℓ, and BrO

B. Marshall L. Ginter
Institute for Physical Science and Technology
University of Maryland
College Park, MD 20742

C. Abstract of Research Objectives. Concern over halogen catalyzed decomposition of O_3 in the upper atmosphere has generated need for data on the atomic and molecular species X, HX and XO (where X is Cℓ and Br). Of special importance are Cℓ produced from freon decomposition and Cℓ and Br produced from natural processes and from other industrial and agricultural chemicals. We have been providing basic spectral and photodissociation data on HCℓ, HBr, and BrO necessary (1) to detect specific states and energy levels, (2) to enable detailed modeling of the processes involving molecular dissociation, ionization, etc., and (3) to help evaluate field experiments to check the validity of model calculations for these species in the upper atmosphere.

D. Summary of Progress and Results. During 1982-83 we have (1) prepared a critical delineation of the complex problem of predissociation in the HX molecules, (2) made a final check of the assignments of our HCℓ atlas for the ∿1100-1500 Å region which we are preparing to submit for publication, and (3) rechecked and finalized a comparable HBr atlas. The complex, variable (with wavelength) problems of dissociation and predissociations in the HX molecules have received major emphasis. The attached RKR potential energy curves for HCℓ illustrates one of the summary results included with the HCℓ atlas.


HCl
90,000 cm⁻¹
85,000 cm⁻¹
80,000 cm⁻¹
75,000 cm⁻¹
1.0 Å
2.0 Å
3.0 Å
$R\,^1\Pi$
$N\,^1\Pi$
$K\,^1\Pi$
$j\,^3\Sigma^-(0^+)$
$I\,^1\Delta$
$H\,^1\Sigma^+$
$i\,^3\Delta_1,\ j\,^3\Sigma^-(1^\pm)$
$i\,^3\Delta_2$
$k\,^3\Pi_1$
$n\,^3\Pi_1$
$E\,^1\Sigma^+$
$g\,^3\Sigma^-(1^\pm),\ G\,^1\Sigma^-$
$g\,^3\Sigma^-(0^+)$
$D\,^1\Pi$
$d\,^3\Pi_i$
$V\,^1\Sigma^+$
$r\,^3\Pi_i$
$M\,^1\Pi$
$m\,^3\Pi_i$
$F\,^1\Delta$
$f\,^3\Delta_i$
$C\,^1\Pi$
$A\,^1\Pi$
$a\,^3\Pi$
$b\,^3\Pi_i$
$t\,^3\Sigma^+$

B. SPECTROSCOPY

A. Title of Research Task:

Spectroscopic Investigations In Support of Stratospheric Experiments

B. Investigators and Institutions:

C. Chackerian, Jr. (NASA-Ames)

R. Boese (NASA-Ames)

F. Bonomo (Univ. of Denver)

G. Guelachvili (Univ. of Paris)

L. Giver (NASA-Ames)

D. Goorvitch (NASA-Ames)

R. Tipping (Univ. of Alabama)

C. Townes (Univ. of California, Berkeley)

F. Valero (NASA-Ames)

P. Varanasi (State Univ. of New York)

T. Wilkerson (Univ. of Maryland)

C. Abstract of Research Objectives:

The purpose of these investigations is to provide the spectroscopic data needed for the detection and quantitative abundance determination of minor constituents in the Earth's stratosphere. Specifically, basic molecular parameters such as absorption line intensities, total absorption band intensities, absorption line half-widths, and pressure induced line positional shifts will be measured. The work is a necessary part of the total stratospheric effort since it will define the spectral regions to be used to detect particular species and the type of spectroscopic instrumentation which should be carried aboard various observing platforms.

D. Summary of Progress and Results:

In addition to the work entailed in the publications listed below (Section E), L. P. Giver et al. have obtained nitric acid band intensities and band model parameters from 610 to 1760 cm^{-1}. Preliminary laboratory work has started to determine the broadening of the pure rotational lines of water and the low temperature broadening of the vibration-rotational fundamental of hydrochloric acid. A short cryogenic absorption cell is currently under construction and a design study is in progress for the construction of a cryogenic multiple reflectance cell suitable for use with our 0.002 cm^{-1} resolution BOMEM Fourier Transform Spectrometer.

E. Journal Publications (1982 - 1983):

1. "Band Model Analysis of the H_2O_2 ν_6(b) Band", D. Goorvitch, F.P.J. Valero, F.S. Bonomo and P.M. Silvaggio, J. Quant. Spectrosc. Rad. Transfer 27, 575-584 (1982).

2. "Water Absorption Lines, 931-961nm: Selected Intensities, N_2-Collision-Broadening Coefficients, Self-Broadening Coefficients, and Pressure Shifts in Air", L.P. Giver, B. Gentry, G. Schwemmer and T.D. Wilkerson, J. Quant. Spectrosc. Rad. Transfer 27, 423-436 (1982).

3. "Direct Retrieval of Lineshape Parameters" Absolute Line Intensities for the ν_2 Band of CH_3D", C. Chackerian, Jr. and G. Guelachvili, J. Mol. Spectrosc. 97, 316-332 (1983).

4. "CO 1-0 Band Isotopic Lines as Intensity Standards", C. Chackerian, G. Guelachvili and R.H. Tipping, J. Quant. Spectrosc. Rad. Transfer. 30, 107-112 (1983).

5. "Vibration-Rotational and Rotational Intensities for CO Isotopes", C. Chackerian, Jr. and R.H. Tipping, J. Mol. Spectrosc. 99, 431-449 (1983).

6. "Thermal Infrared Lines of Methane Broadened by Nitrogen at Low Temperatures", P. Varanasi, L.P. Giver and F.P.J. Valero, J. Quant. Spectrosc. Rad. Transfer (in press).

7. "Measurements of Nitrogen-Broadened Line Widths of Acetylene at Low Temperatures", P. Varanasi, L.P. Giver and F.P.J. Valero, J. Quant. Spectrosc. Rad. Transfer (in press).

8. "Infrared Absorption by Acetylene in the 12-14 Micron Region at Low Temperatures", P. Varanasi, L.P. Giver and F.P.J. Valero, J. Quant. Spectrosc. Rad. Transfer (in press).

LABORATORY SPECTROSCOPY IN SUPPORT OF ATMOSPHERIC MEASUREMENTS

P.I., Thomas J. McGee
Co-I, William S. Heaps

NASA/Goddard Space Flight Center
Laboratory for Planetary Atmospheres
Greenbelt, Maryland 20771

ABSTRACT

The laboratory objective is to provide spectroscopic data necessary to interpret results from atmospheric measurements as well as establish the feasibility of new techniques. The primary function is related to current and proposed LIDAR measurements. Quantitative spectroscopic data such as absorption cross-sections, branching ratios, Franck-Condon factors, lifetimes, and quenching ratios are currently being measured in the laboratory.

Laboratory Spectroscopy in Support of Atmospheric Measurements

The laboratory is involved in several experiments to better understand existing atmospheric data as well as test the feasibility of new field measurements. We have recently completed three separate studies, one calculating OH absorption coefficients from experimental data, another making an experimental determination of the two photon absorption cross-section in NO, and a third measuring absorption cross-section in SO_2 at room and dry ice temperatures.

Because OH is not a stable molecule it is difficult to produce in well-known number densities, making direct cross-section measurements difficult. We have taken experimentally determined lifetimes and branching ratios, and related these to the absorption cross-section. Cross-sections for transitions arising from low lying rotational levels have been calculated for both the (0,0) and (0,1) manifolds. Effective cross-sections have also been calculated taking into effect the Doppler width of the transition and the spectral linewidth of the laser excitation source. These values have been used in the interpretation of returns from the GSFC balloon LIDAR OH experiment.

The two photon NO work is a result of a program to assess the feasibility of two photon laser induced fluorescence as an atmospheric measurement tool. The experiment in NO was a novel approach using four-waving mixing in NO and Coherent Anti-Stokes Raman Scattering (CARS) in N_2 to measure the parameters necessary to extract the two photon absorption coefficients. The results indicate that two photon techniques provide the necessary sensitivity for atmospheric measurements under certain circumstances. The current state of laser technology is still the limiting factor in designing such a field experiment.

Additionally the emission spectra from the v'=0 and 1 levels in NO have been analyzed spectrally, for branching ratios and Franck-Condon factors. The data from the v'=0 level has been used to design a LIDAR experiment to measure NO in the atmosphere. Data from both levels are being used to interpret spectrally resolved Nimbus-7 data in an effort to extract NO concentrations in the upper stratosphere and mesosphere.

SO_2 absorption cross-sections became important as a result of the recent eruption of El Chichon, which injected large quantities of SO_2 and CS_2 directly into the stratosphere. SO_2 absorbs in the same spectral regions that ozone monitoring instruments aboard Nimbus-7 use to measure ozone levels and the SO_2 plume from the volcano was mapped by the TOMS instrument aboard Nimbus-7. Cross-sections for SO_2 were measured for 3000 Å to 3200 Å at both room and dry ice temperatures. These are the first low temperature measurements to be made and indicate small spectral shift as well as changes in intensity as a result of population redistribution in the ground state.

Recent Publications

"Fluorescence branching ratios from the $A^2\Sigma^+(v'=0)$ state of NO", T. J. McGee, G. E. Miller, J. Burris, Jr., and T. J. McIlrath, JQSRT, 29, 333, 1983.

"A two photon absorption cross-section measurement in nitric oxide", J. Burris, Jr., T. J. McIlrath, and T. J. McGee, accepted for publication, Chem. Phys. Lett., July 1983.

"Absolute OH absorption cross-sections for LIDAR measurements", T. J. McGee, and T. J. McIlrath, JQSRT, accepted for publication, August 1983.

Summary Report

A. Title: "Laboratory Study of Resonance Fluorescence in Atmospheric Gases"

B. Investigator: T. J. McIlrath
Institute for Physical Science and Technology
University of Maryland
College Park, Md. 20740

C. Abstract of Objectives:

Both fluorescence and DIAL Lidar have become important tools for remote sensing in the upper atmosphere. Recent experiments with a balloon borne lidar have demonstrated the feasibility of fluorescence measurements of OH radicals and DIAL measurements of O_3. The feasibility of making lidar measurements is dependent on both complete spectroscopic data of the species being studied and development of laser and auxiliary systems at the appropriate wavelengths. This program is designed to work on these support aspects of the lidar program. Fluorescence studies of NO and NO_2 molecules have been carried out to allow an evaluation of their suitability for fluorescence lidar detection. Absolute fluorescence yields have been obtained and they provide the basis for current work on modeling of lidar under stratospheric conditions. In support of lidar systems we are developing a source of tunable infrared radiation using stimulated Raman scattering and a tunable dye laser. We are also working on wavemeter development to provide absolute wavelength control and we are constructing components for the platform of a balloon born lidar system to be flown by GSFC.

D. Summary of Progress and Results:

Studies of NO_2 fluorescence cross-section were completed for excitation at 5320Å and 4161Å using N_2 and O_2 as quenching gases. The 4161Å radiation was obtained by stimulated Raman scattering of the 3547Å third harmonic of a Nd:YAG laser in high pressure H_2 gas and it provides excitation to just below the predissociation threshold. Absolute quantum yields were obtained in the collision free mode and these results are being submitted for publications. The cross-sections for fluorescence as a function of wavelength have been obtained from the excitation wavelength to 7000Å. It has been found that the Stern-Volmer plots for the fluorescence intensity are linear up to 10 torr pressure. The cross-section information is being prepared for publication. The cross-section data has been assembled along with Rayleigh scatter background signals and a model is being prepared for the signal-to-noise ratio expected in stratospheric lidar experiments.

The NO molecule has been extensively studied using both single photon and two photon excitation. The single photon excitation has allowed an accurate measurement of the branching ratios in fluorescence into various ground vibrational states. A reprint of this work is attached. The two-photon studies were aimed at measuring the absolute excitation cross-section. Excitation using two photons would allow lidar operation at more convenient and efficient laser wavelengths. This work has been completed and resulted in a Ph.D. Thesis. The results have been submitted for publication and a preprint is enclosed. Two more papers are in the process of preparation.

A summary of excitation cross-sections for OH in a form directly applicable to lidar measurements has been prepared and accepted for publication. A preprint is attached. Measurements of Xe excited state lifetimes are being prepared for publication.

A Fizeau wavemeter constructed by CNRS and designed to monitor wavelengths near 5600Å (twice the OH resonance frequency) has been analyzed and a modified version is being prepared for use at near infrared wavelengths which characterize H_2O absorption features. A stimulated Raman scattering system has been constructed and tested and will be used in conjunction with dye lasers operating between 5500Å and 7000Å to provide an excitation system appropriate to transitions between 7000Å and 10,000Å with special interest in H_2O absorption lines. Finally we have participated in the construction of the GSFC balloon lidar platform. The work done under this program has been done in conjunction with the GSFC laboratory and field lidar programs and with scientists at GSFC.

E. Publications

1. T. J. McGee and J. Burris, Jr., Appl. Optics 20, 3483 (1981). "$CF_2C\ell_2$ as a dye laser tuning gas: refractive-index measurements".
2. T. J. McGee, J. Burris, Jr., T. J. McIlrath and G. E. Miller, J. Quant. Spectrosc. Radiat. Transfer 29, 333 (1983). "Fluorescence Branching Ratios from the $A^2\Sigma^+(v'=0)$ State of NO".
3. T. J. McGee and T. J. McIlrath, "Absolute OH Absorption Cross Sections for Lidar Measurements". Accepted for publication in J. Quant. Spectrosc. Radiat. Transfer.
4. J. Burris, Jr., T. J. McIlrath and T. J. McGee. "A Two Photon Absorption Cross-Section Measurement in Nitric Oxide". Submitted to Chem. Phys. Lett.
5. C. S. Dulcey, "A Study of Laser-Induced Fluorescence Cross-Sections in Nitrogen Dioxide". Ph.D. Thesis, University of Maryland (1982).
6. J. Burris, Jr., "A Two Photon Absorption Cross-Section Measurement in the Gamma Band System of Nitric Oxide", Ph.D. Thesis, University of Maryland (1982).

RESEARCH TASK SUMMARY

A. Title of Research Task

"High Resolution Ultraviolet Cross Section Measurements of Ozone"

B. Investigators and Institutions

Principal Investigator:	W.H. Parkinson Harvard College Observatory Cambridge, MA 02138
Co-Investigator:	D.E. Freeman Harvard College Observatory Cambridge, MA 02138
Co-Investigator:	K. Yoshino Harvard College Observatory Cambridge, MA 02138

C. Abstract of Research Objectives

The objective is to perform laboratory measurements at high resolution of the absorption cross sections of the Hartley-Huggins bands of ozone, which occur in the wavelength region 200-370 nm, at temperatures of stratospheric interest, 200-300 K. Special attention will be paid to cross sections in (a) the fall-off region 295-370 nm where the discrete structure is most pronounced and the temperature dependence most marked; this region includes wavelengths near 305.5 nm where possible errors in the effective cross section are thought responsible for errors in Dobson ozone determinations and (b) the region near 200 nm where significant solar transmission windows occur in the atmosphere and where previous measurements differ considerably. The high resolution measurements to be made with a 6.65 m scanning spectrometer having an instrumental width of 0.003 nm will remedy deficiencies in past work arising from the limited resolutions, $\sim$0.05 nm, previously used. These new measurements on ozone are needed for the determinations of the amount of solar ultraviolet radiation reaching the Earth's surface, and for the determination of the quantum yield of O ^{1}D as a function of wavelength and temperature.

D. Summary of Progress

Cross sections of the Hartley-Huggins bands of O_3 at the temperature 195 K have been obtained from photoabsorption measurements at column densities in the range 2×10^{17} - 1×10^{21} cm^{-2} throughout the wavelength region 240-350 nm with a 6.65 m photoelectric scanning spectrometer equipped with a 2400 lines mm^{-1} grating and operated at an instrumental width of 0.003 nm. The assumption made in putting the measured relative cross sections on an absolute basis have been investigated. Fine structure in the cross section of the Huggins bands has been measured in the region 323-327 nm where shallow features of width 0.01-0.02 nm, observed for the first time, occur superposed on a stronger apparent continuum exhibiting broader wavy structure.

E. Journal Publications, 1982-1983

D.E. Freeman, K. Yoshino, J.R. Esmond and W.H. Parkinson, "High Resolution Absorption Cross Section Measurements of Ozone at 195 K in the Wavelength Region 240-350 nm," Planetary and Space Science, accepted for publication (June 1983).

553-F-84

Determination of the Temperature Dependence of the Absorption Cross-Sections of Ozone

Arnold M. Bass
National Bureau of Standards

Abstract

The ultraviolet absorption cross-sections of ozone, as required for stratospheric measurements and model calculations, are being measured as a function of temperature. Measurements have been completed for several temperatures between 295K and 203K over the wavelength region 220 nm to 350 nm.

Summary of Progress and Results

The data available in the literature on the UV absorption cross-sections of ozone, and which are principally used for the interpretation and analysis of atmospheric ozone, were published more than twenty years ago. There are serious gaps in the published data, and there are indications of internal inconsistencies in the data. To improve on the data base for this problem we have been remeasuring the ozone cross-sections with much improved technical procedures.

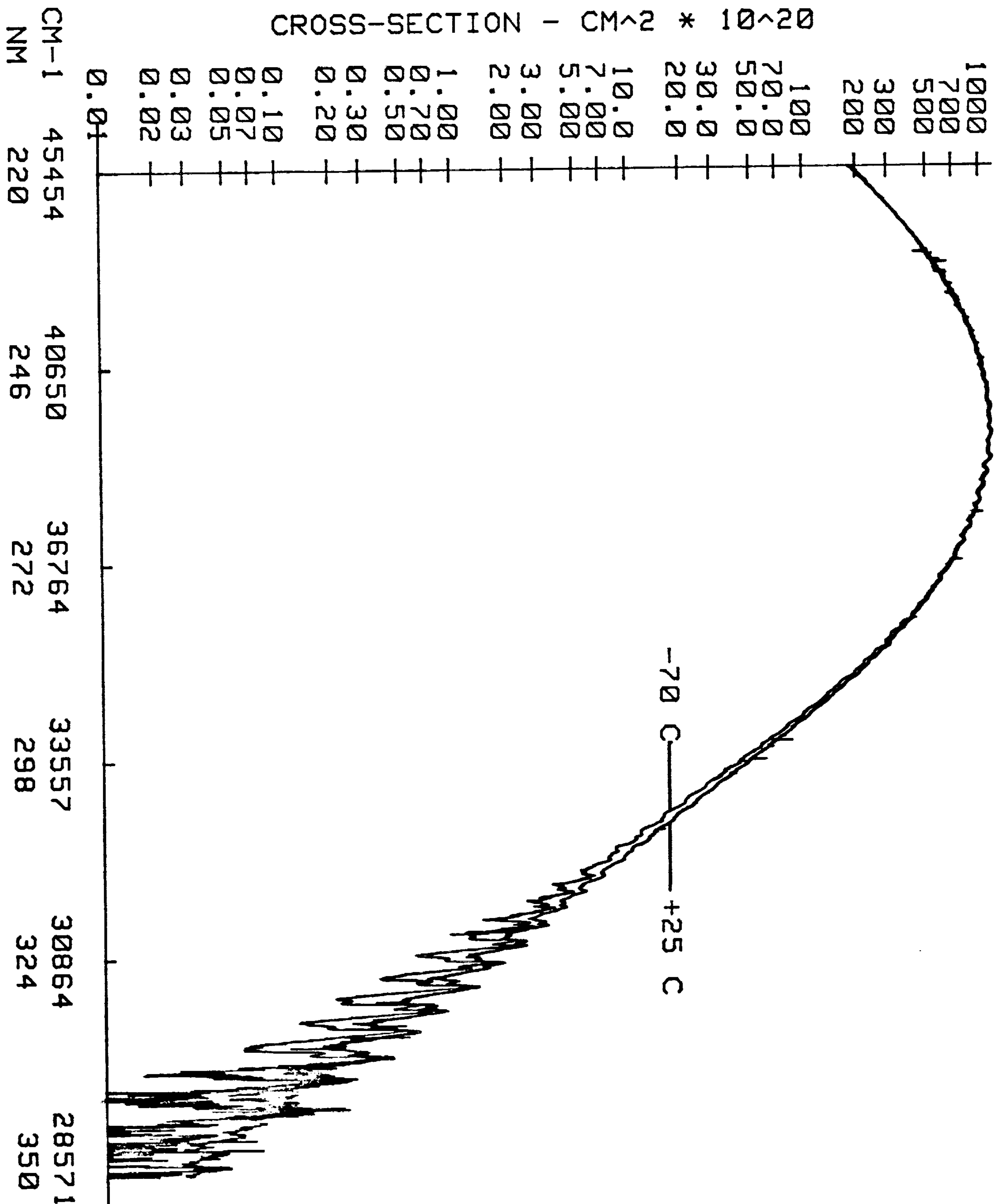
The present work concentrates on the wavelength region from 220 to 350 nm and includes the Hartley bands and the Huggins bands of the ozone spectrum. Our measurements have been made with a spectral resolution of 0.025 nm in steps of 0.050 nm. This resolution is adequate to map accurately the observed structure in the spectrum. Over this region we have recorded the spectrum at temperatures between 295K and 203K: (measurements have been made at 203, 218, 230, 243, 273, and 295K). Our measurements, which have been made with very high photometric accuracy, are referenced to the accepted value for the absorption cross-section at 253.7 nm (1.146×10^{-17} cm^2).

The attached figures indicate typical results we are obtaining from this program. Figure 1 shows the ozone absorption spectrum from 220 to 350 nm at the maximum and minimum temperatures (-70C and +25C). Figure 2 shows the region from 320 to 330 nm at higher spectral resolution, at five measurement temperatures (-70, -55, -30, 0, +25C). Figure 3 shows the temperature dependence of the ozone absorption cross-section at two of the Dobson wavelengths; the cross-section was integrated over the nominal Dobson slit function.

The detailed results of this work are now being prepared for publication. Preliminary application of the data has proven useful in: (a) resolving erroneous speculations about the presence of high concentrations of SO_2 in the stratosphere; and (b) resolving some internal inconsistencies in the analysis of Dobson ozone measurements.

Publications:

1. "Anomalous Atmospheric Spectral Features Between 300 and 310 nm Interpreted in Light of New Ozone Absorption Coefficient Measurements" R.D. McPeters and A.M. Bass, Geophys. Res. Lett., 9 (227-230) 1982.


CROSS-SECTION - CM^2 * 10^20
1000
700
500
300
200
100
70.0
50.0
30.0
20.0
10.0
7.00
5.00
3.00
2.00
1.00
0.70
0.50
0.30
0.20
0.10
0.07
0.05
0.03
0.02
0.01
CM-1
NM
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40650
246
36764
272
33557
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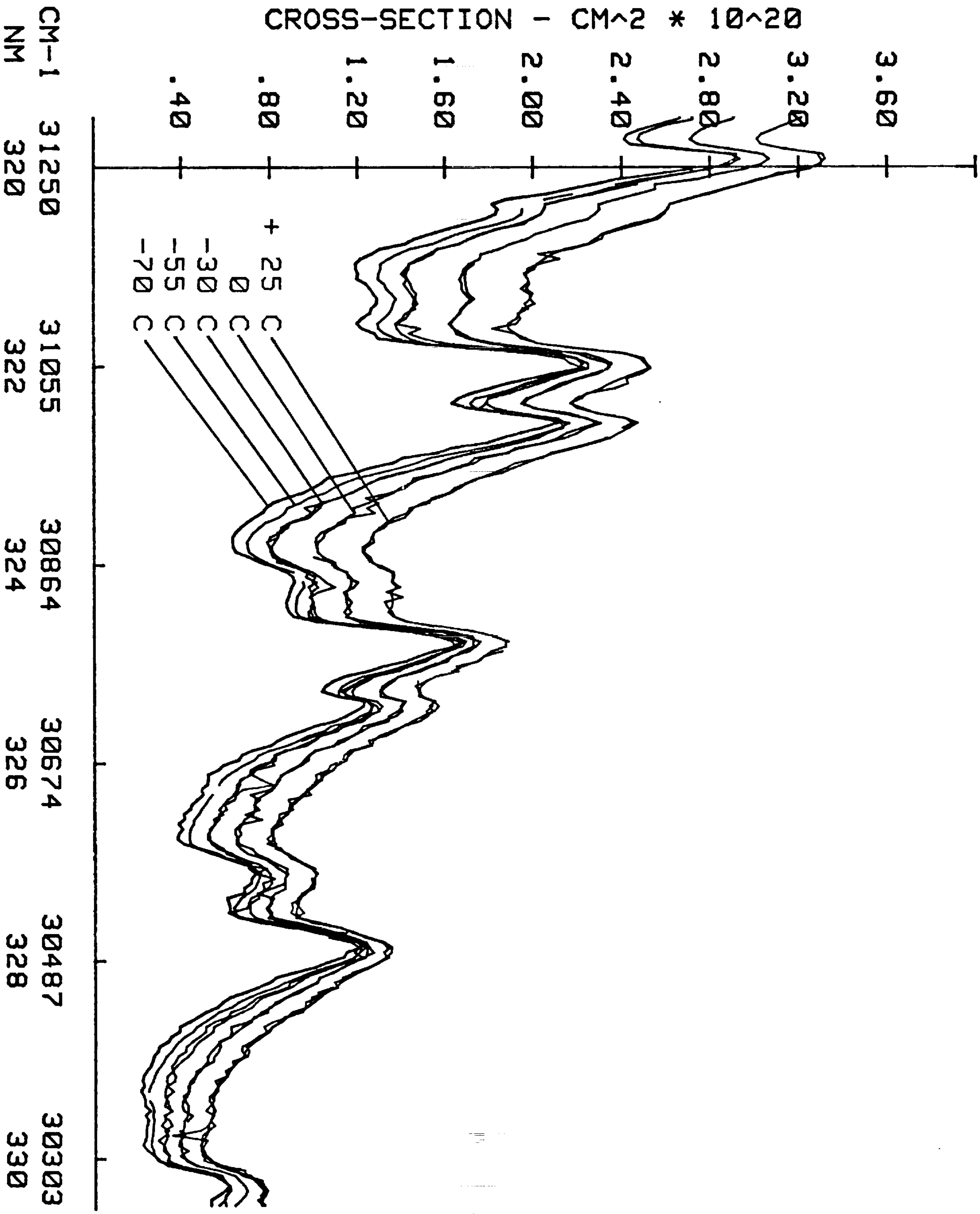
28571
350
-70 C
+25 C

Figure 1


CROSS-SECTION - CM^2 * 10^20
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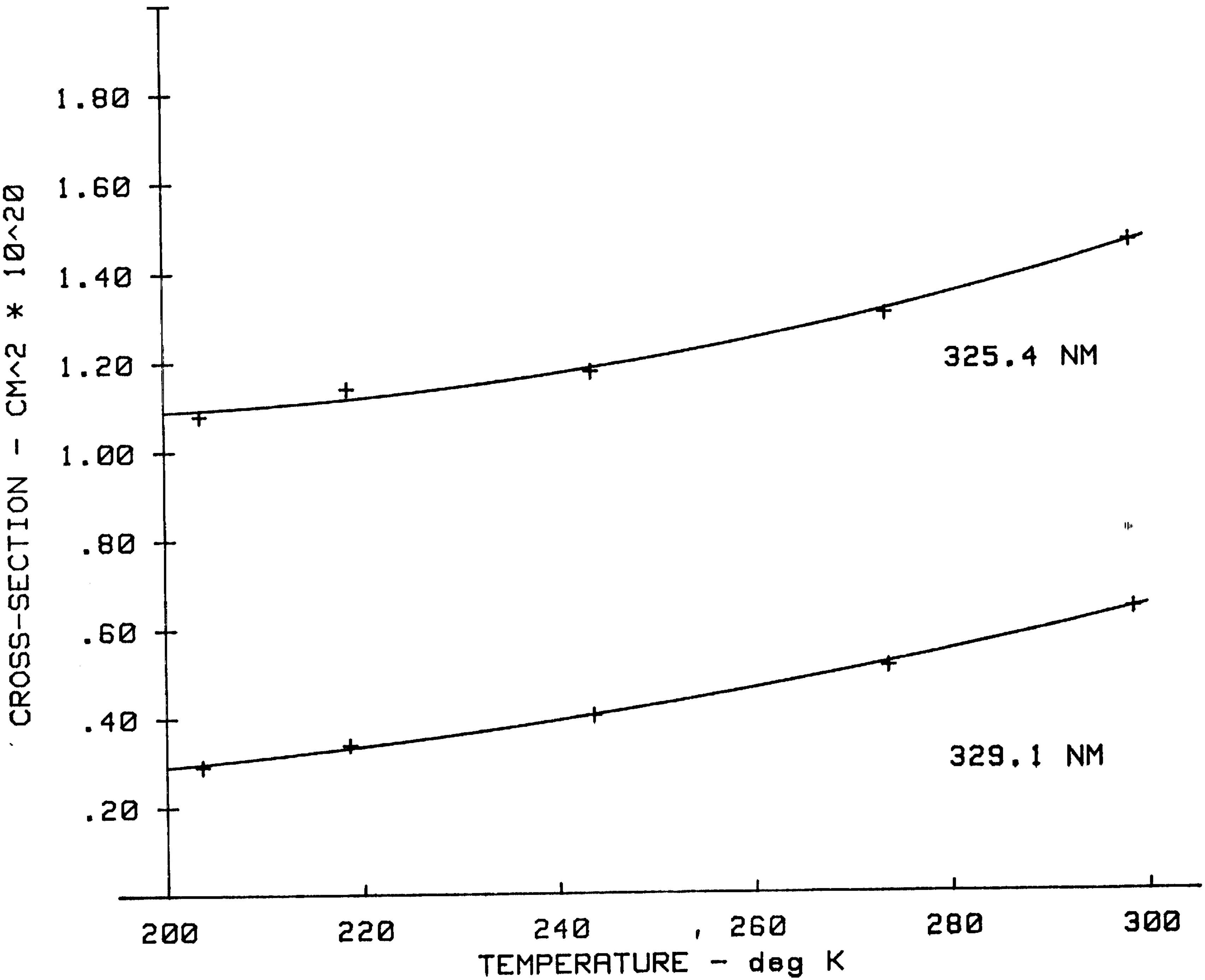
3.20
2.80
2.40
2.00
1.60
1.20
.80
.40
CM-1
NM
31250
320
31055
322
30864
324
30674
326
30487
328
30303
330
+ 25 C
0 C
-30 C
-55 C
-70 C

Figure 2


CROSS-SECTION - CM^2 * 10^20
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1.60
1.40
1.20
1.00
.80
.60
.40
.20
325.4 NM
329.1 NM
200
220
240
260
280
300
TEMPERATURE - deg K

Figure 3

E. Journal Publications, 1982-1983

K. Yoshino, D.E. Freeman, J.R. Esmond and W.H. Parkinson, "High Resolution Absorption Cross Section Measurements and Band Oscillator Strengths of the (1,0)-(12,0) Schumann-Runge Bands of O_2," Planetary and Space Science 31, 339-353 (1983).

K. Yoshino, D.E. Freeman and W.H. Parkinson, "Atlas of the Schumann-Runge Absorption Bands of O_2 in the Wavelength Region 175-205 nm," Journal of Physical and Chemical Reference Data," accepted for publication (August 1983).

RESEARCH TASK SUMMARY

A. Title of Research Task

"Determination of Band Oscillator Strengths of Atmospheric Molecules from High Resolution Vacuum Ultraviolet Cross Section Measurements"

B. Investigators and Institutions

Principal Investigator:	W.H. Parkinson Harvard College Observatory Cambridge, MA 02138
Co-Investigator:	D.E. Freeman Harvard College Observatory Cambridge, MA 02138
Co-Investigator:	K. Yoshino Harvard College Observatory Cambridge, MA 02138

C. Abstract of Research Objectives

The objective is to perform laboratory measurements at high resolution of the vacuum ultraviolet absorption cross sections of the atmospherically important Schumann-Runge bands of molecular oxygen which occur in the wavelength region 175-205 nm, and to derive the band oscillator strengths and predissociation line widths from the measured cross sections. Accurate cross sections for oxygen are required to determine the intensity of solar radiation that penetrates to particular atmospheric altitudes and is available for absorption by and dissociation of stratospheric constituents or pollutants such as nitric oxide and chlorofluoromethanes.

D. Summary of Progress

(a) A 6.65 m photoelectric scanning spectrometer/spectrograph has been used to perform high resolution absorption cross section measurements of O_2 at 77 K throughout the wavelength region 175-205 nm. The temperature 77 K is chosen for the spectral simplification it achieves by eliminating bands and continuum from $v'' = 1$ levels. Comparison of the band oscillator strengths being obtained from these measurements with our previous values for O_2 at 300 K permits study of the temperature dependence.

(b) From high resolution spectra of the absorption wavelengths of O_2 at 300 K, a photographic atlas showing detailed vibration-rotation assignments of the Schumann-Runge absorption bands has been prepared. Significantly improved molecular spectroscopic constants of O_2 result from these data.

REPORT ON THE TASK "PROPOSAL TO TAKE AND ANALYZE THE INFRARED SPECTRUM OF THE $\nu_2 + \nu_6$ BENDING COMBINATION BAND OF HYDROGEN PEROXIDE AT 2649 cm^{-1}."

BY

WILLIAM BRUCE OLSON AND JON T. HOUGEN
MOLECULAR SPECTROSCOPY DIVISION
NATIONAL BUREAU OF STANDARDS
WASHINGTON, DC 20234

Research Objectives.

The final objective of this investigation is to provide an absorption line listing of the vibrational-rotational transitions, giving precise wavenumber positions, intensities, and assignments, for the relatively strong bending combination mode of hydrogen peroxide at 2649 cm^{-1}. The ground rotation-torsional state has proved to be inadequately characterized by previous work and several other objectives associated with understanding this state must be accomplished in order to meet the final goal.

Summary of Progress and Results.

We have built a White cell, taken all the necessary data, which we expect to have in convenient form by the end of October, 1983; we have verified a perturbation in the ground state and have obtained a preliminary value of the interaction constant, and have extended assignments in the vibrational bending combination band. We will elaborate on these points in the following two subsections.

I. Data Taking and Data Reduction:

A White-type multiple reflection absorption cell designed to hold hydrogen peroxide was constructed at NBS and used to obtain spectra of hydrogen peroxide of .01 cm^{-1} resolution on the Fourier Transform Spectrometer at Kitt Peak National Observatory in collaboration with Dr. James Brault. In December of 1982, spectra at about 2 mm. pressure were taken with and without N_2O for calibration at path lengths of 7 and 28 m over two overlapping spectral regions spanning the range from 2386 cm^{-1} to 3900 cm^{-1}. The large number of absorption lines obtained has proved too large to manage efficiently with software available at NBS or NASA-Goddard Space Flight Center. A data file of 7 m pathlength has been apodized and the absortion peaks found from 2386 to 2972 cm^{-1} by Dr. Donald Jennings of NASA-Goddard. In this region there are about 10,000 lines with absorption greater than 1%.

Agreement has been reached with Dr. Linda Brown of JPL to provide apodized plots of spectra, and both hard copy and magnetic tape listing of absorption peak positions and intensities during October 1983. Data transfer and storage and plotting problems greatly hindered the progress in the analysis reported in the next sub-section.

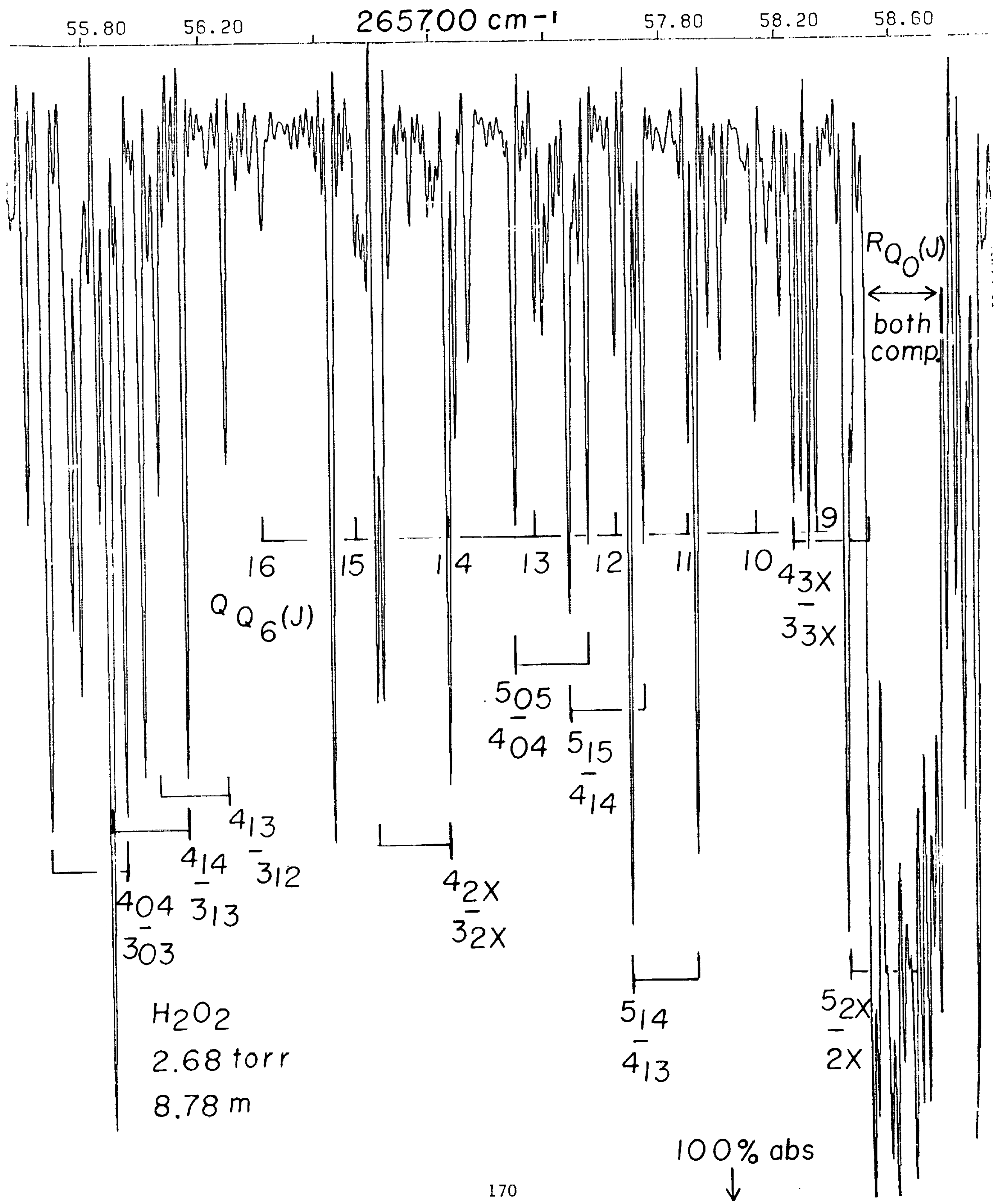
II. Progress in Analysis:

In 1965 Hunt, Leacock, Peters, and Hecht reported that there was a perturbation of the ground torsional state by the first excited torsional state. This result came from both their model for the torsional problem and direct evidence in their medium resolution far infrared spectra. Subsequent extensive submillimeter data have been of too low values of the K rotational quantum number to provide any information on this problem. We have entered into collaboration with Prof. Robert Hunt in order to get adequate data for the complete characterization of this perturbation. We have confirmed this perturbation from extensive single line assignments made in high resolution spectra in the 3600 cm^{-1} region by Prof. Hunt and computer fitting at NBS. A preliminary report of this result and a preliminary experimental value for interaction constant was given at the Ohio State University Molecular Spectroscopy Symposium in June 1983. The preliminary experimental interaction constant we have obtained agrees reasonably well with that resulting from the torsional model of Hunt, Leacock, Peters, and Hecht. Longer path spectra is needed by Prof. Hunt in order to make higher J, and K assignment and eventually get a very good value for the interaction constant, and we took the required spectra along with that of the bending combination at Kitt Peak in December of 1982.

In spite of our present lack of plots of apodized spectra and line lists of high precision, we have unapodized spectrum plots and line lists of moderate precision and have been able to greatly extended assignments in both parallel and perpendicular components from both torsional ground states in the combination bending mode of hydrogen peroxide. From calculated energy levels with K less than or equal to 6 where the effects of the ground state perturbation are small, one can from one correct assignment in either the parallel or perpendicular component of one torsional state calculate several other parallel and perpendicular transitions. In this manner we have been able to make several hundred assignments, which await only precise wavenumber positions for accurate fitting to begin.

Figure Caption.

Figure 1. A short section of unapodized fourier transform infrared spectrum of H_2O_2 in the combination bending mode, $\nu_2 + \nu_6$, just above the band origin at 2649.014 cm^{-1}. For the R-branch transitions in the parallel components of the bands, the short vertical lines on the horizontal tie-bars locate the assigned transitions. The left line arises from the τ=1,2 component of the ground torsional state, and the right one arises from the τ=3,4 component of the ground torsional state, whose band origin is at 2649.269 cm^{-1}. The overlapped $^{R}Q_0(J)$ branches of both torsional components of the perpendicular bands are indicated on the right in the figure. The Q-branch lines indicated are those of the lower torsional component only.


55.80
56.20
265700 cm-1
57.80
58.20
58.60
RQ0(J)
both comp.
16
15
14
13
12
11
10
9
QQ6(J)
43X - 33X
505 - 404
515 - 414
413 - 312
414 - 313
404 - 303
42X - 32X
514 - 413
52X - 2X
H2O2
2.68 torr
8.78 m
100% abs

A. TITLE:

Infrared Laboratory Spectroscopy in Support of Stratospheric Measurements
Infrared Laboratory Spectroscopy in Support of ATMOS

B. INVESTIGATORS:

Dr. Robert A. Toth (P.I.), Jet Propulsion Laboratory
Dr. Linda R. Brown (Co.I.), Jet Propulsion Laboratory

C. RESEARCH OBJECTIVES:

The objective of this program is the acquisition and analysis of molecular spectral parameters for the 2 to 16 μm region in order that data obtained from stratospheric measurements programs can be properly interpreted. The parameters derived from this research include the line positions, line strengths, line widths, and transition assignments of molecules present in the stratosphere. The gases studied fall into two general categories:

1. Molecules (such as CH_4, CO_2, H_2O) which produce absorptions so strong that lack of detailed knowledge of their line parameters would hinder the detection of other trace gases.

2. Less abundant trace gases which are expected to produce weak features in the stratospheric spectrum (such as H_2CO, NO_2, COF_2, $CH_3C\ell$).

The molecules of the first category have strong absorptions over wide expanses of the stratospheric spectrum so that compilation of good line parameters require the analysis of several vibration-rotation bands. Once completed, however, the work on the second category can be done readily since one needs to analyze only the few strong bands of the trace gases that are not overlapped by transitions of other molecules.

D. SUMMARY OF PROGRESS AND RESULTS:

In FY 82 and FY 83, laboratory spectra were obtained with a Fourier Transform Spectrometer (FTS) at the Kitt Peak National Observatory (KPNO). Data that have been obtained include spectra of N_2O, H_2O, HDO, NO_2, CH_4, H_2CO. During FY 83, additional software for the ATMOS computing facility was implemented and tested. The software is designed to obtain molecular line parameters (line positions, strengths, widths) by a non-linear least squares procedure that iterates between an observed spectrum and a synthetic spectrum calculated at correct instrumental and gas conditions. Measurements with spectra from the Kitt Peak spectrometer can be made with accuracies of ± 0.0005 cm^{-1} or better for positions and 1% to 2% for strengths and widths of unblended absorptions. This process has been successfully applied to a number of molecules including CH_4, HDO, N_2O and NO_2. Parameter lists for H_2O, HDO and CH_4 have already been incorporated in the 1982 version of the Air Force Geophysical Laboratory (AFGL) compilations.

E. PUBLICATIONS:

1. L. R. Brown, "Line Strengths of the $\nu_1 + \nu_4$ Band of $^{12}CH_4$," J. Mol. Spectrosc. 96, 94-105 (1982).

2. L. R. Brown, J. S. Margolis, R. H. Norton amd B. Stedry, "Computer Measurement of Line Strengths with Application to the Methane Spectrum," Appl. Spectrosc. 37, 287-292 (1983).

3. L. R. Brown and L. S. Rothman, "Methane Line Parameters for the 2.3 μm Region," Appl. Optics 21, 2425-2427 (1982).

4. L. R. Brown, R. A. Toth, R. H. Hunt and J. W. Brault, "Line Assignments and Intensities of the $\nu_2 + \nu_3 - \nu_2$ Band of $^{12}CH_4$," J. Mol. Spectrosc. 89, 528-541 (1981).

5. C. Camy-Peyret, J.-M. Flaud and R. A. Toth, "Line Positions and Intensities for the $2\nu_2$, ν_1 and ν_3 Bands of $H_2{}^{17}O$," Molecular Physics 42, 595-604 (1981).

6. C. Camy-Peyret, J.-M. Flaud and R. A. Toth, "The Interacting States (020), (100) and (001) of $H_2{}^{17}O$ and $H_2{}^{18}O$," J. Mol. Spectrosc. 87, 233-244 (1981).

7. R. H. Hunt, J. E. Lolck, A. G. Robiette, L. R. Brown and R. A Toth, "Measurement and Analysis of the Infrared Absorption Spectrum of the $2\nu_2$ Band of $^{12}CH_4$," J. Mol. Spectrosc. 92, 246-256 (1982).

8. L. R. Brown, R. A. Toth, A. G. Robiette, J.-E. Lolck, R. H. Hunt and J. W. Brault, "Analysis of the ν_1 and $\nu_2 + \nu_4$ Bands of $^{12}CH_4$," J. Mol. Spectrosc. 93, 317-350 (1982).

9. R. A. Toth, V. D. Gupta and J. W. Brault, "Line Positions and Strengths of HDO in the 2400-3300 cm^{-1} Region," Appl. Optics 21, 3337 (1982).

10. R. A. Toth and J. W. Brault, "Line Positions and Strengths in the (001), (110) and (030) Bands of HDO," Applied Optics 22, 908 (1983).

11. L. S. Rothman, R. R. Gamache, A. Barke, A. Goldman, J. R. Gillis, L. R. Brown, R. A. Toth, J.-M. Flaud and C. Camy-Peyret, "AFGL Atmospheric Absorption Line Parameters Compilation: 1982 Edition," Applied Optics 22, 2247 (1983).

12. J. E. Lolck, A. G. Robiette, R. H. Hunt and L. R. Brown, "Molecular Constants for the Interacting States of the ν_1, ν_3, $2\nu_2$, $\nu_2 + \nu_4$, $2\nu_4$ Bands of $^{12}CH_4$," J. Mol. Spectrosc. 92, 229 (1982).

A. LABORATORY SPECTROSCOPY FOR LASER REMOTE SENSING OF THE EARTH'S ATMOSPHERE

B. Investigators: Christopher R. Webster
Jack S. Margolis
Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, CA 91109

C. Abstract of Research Objectives

The objective of this task is to obtain and analyze spectroscopic data, including accurate line positions, line strengths, and air broadened widths, which are relevant to the detection and measurement of molecules that are important in the photochemical processes occurring in the Earth's atmosphere. These data are especially selected to provide aid in designing and interpreting observations of the atmosphere involving laser instruments.

D. Summary of Progress and Results

The spectrum of ozone in the 900-1250 cm^{-1} region has been measured and analyzed. The N_2-broadened half-widths of many lines of ozone in this region were measured using spectra obtained with tunable diode lasers and with the Kitt Peak one meter Fourier Transform Spectrometer. At the same time accurate line positions for several thousand ozone lines were obtained and compared to those published in the AFGL list. Remarkably good agreement between the two lists obtained for many lines with some notable discrepancies. The relative intensities of the lines in the AFGL list compare favorably to the observations, but there are again some notable discrepancies which are due to interactions between the ν_1 and ν_3 bands and which were evidently not accounted for in computing the AFGL list. A new analysis undertaken in collaboration with Herbert Pickett is underway and already there is improved agreement between computed and observed strengths.

An apparatus for generating HO_2NO_2 using the NO_2BF_4 nitrating reaction with H_2O_2 has been designed and constructed. This generator will produce HO_2NO_2 at high concentrations with minimum impurities (< 10% HNO_3) for survey spectra on the Bomem and TDL spectrometers.

Detection of NH_3 and NO_2 (at 9.5 μm and 6.2 μm, respectively) in the infrared region using TDL sources, and of the I^- negative ion using a dye laser source, has been achieved using optogalvanic detection. These studies represent the first time this technique has been used to detect negative ions and the first molecular spectra observed in the infrared region. This work will form the basis for assessing the possible use of optogalvanic techniques to provide direct wavelength calibration for atmospheric sensing of reactive species using tunable laser sources.

E. Journal Publications

1. "Measurements of Pressure-Broadening Coefficients of NO and O_3 Using a Computerized Tunable Diode Laser Spectrometer", S. Lundqvist, Jack S. Margolis, J. Reid; Applied Optics 21, 3109 (1982).
2. "Computer Measurements of Line Strength With Application to Methane Spectrum", Linda R. Brown, Jack S. Margolis, Robert H. Norton, Barbara D. Stedry; Applied Spectroscopy 37, 287 (1983).
3. "N_2 Broadening Parameters of Ozone at 9.6 μm", Jack S. Margolis; J. Quant. Spectrosc. and Rad. Transf. 29, 539 (1983).
4. "Optogalvanic Wavelength Calibration for Laser Monitoring of Reactive Atmospheric Species," C. R. Webster, Applied Optics 21, 2298 (1982).
5. "Laser Optogalvanic Spectroscopy of Molecules," C. R. Webster and C. T. Rettner, Laser Focus 19, No. 2, 41 (1983).
6. "Infrared Laser Optogalvanic Spectroscopy of Molecules," C. R. Webster and R. T. Menzies, J. Chem. Phys. 78, 2121 (1983).
7. "Laser Optogalvanic Photodetachement Spectroscopy: A New Technique for Studying Photodetachment Thresholds with Application of I^-," C. R. Webster, I. S. McDermid, and C. T. Rettner, J. Chem. Phys, 78, 646 (1983).

A. Title of Research Task

Millimeter and Submillimeter Spectroscopy in Support of Upper Atmospheric Research

B. Investigators and Institutions

Edward A. Cohen
Herbert M. Pickett
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

C. Abstract of Research Objectives

This program provides millimeter and submillimeter frequencies, linewidths and transition moments of upper atmospheric species either being sought by the various observing programs or having the potential of being observed by instrumentation under development by NASA. In particular this program directly supports the Microwave Limb Sounders which have flown on aircraft and balloon and which are being developed to fly on the Upper Atmospheric Research Satellite. In addition it supports the development of submillimeter radiometers and provides useful spectroscopic parameters to the infrared spectroscopy programs.

D. Summary of Progress and Results for 1982-83

The accomplishments of the program for 1982-83 are listed along with their relevance to the Upper Atmospheric Research Program.

1. The millimeter and submillimeter spectra of HOCl. This has provided frequency measurements from 8 to 614 GHz, precise determination of both components of the dipole moment, and accurate prediction of line positions and intensities up to 3 THz. This allows one to accurately relate HOCl abundance to its atmospheric spectrum.

2. The millimeter and submillimeter spectra of O_3. This is an extensive task to accurately predict all observable transitions of O_3 to the upper atmospheric millimeter spectrum. The major accomplishments are as follows:

   a. O_3 ground vibrational state. This portion of the task is complete and involved measurement of very high energy rotational transitions and simultaneous analysis of term values determined from very high resolution infrared data. All presently observable rotational transitions of this state are well predicted.

   b. O_3 ν_1, ν_3 excited states. The millimeter spectral measurements have been greatly extended and simultaneously fit with infrared spectra to an improved molecular model. This has provided the first adequate extensive prediction of the millimeter and submillimeter spectra of these states. In addition the infrared line positions and intensities have been accurately determined.

c. O_3 ν_2 and $2\nu_2$ excited states. The millimeter measurements have been extended to allow adequate prediction of atmospheric spectral contributions from these states.

d. Mono ^{17}O ozones. The millimeter spectra of these less abundant O_3 species have been measured for the first time and the analysis is completed.

3. HNO_3 spectra. Computer programs used for the JPL Submillimeter, Millimeter and Microwave Spectral Line Catalogue have been used to explain HNO_3 spectra observed with the NASA balloon-borne FIR spectrometer.

E. Publications 1982-83

E. A. Cohen and H. M. Pickett, Rotational Spectra and Hyperfine Interactions of the Mono ^{17}O Substituted Ozones, J. Mol. Struct. 97, 97-100 (1983)

A. Title of Research Task

High Resolution Spectroscopy to Support Atmospheric Measurements

B. Investigators and Institutions

Principal Investigator: Dr. Mary Ann H. Smith
Co-Investigators: Dr. Robert S. Rogowski
Mr. James M. Hoell
Dr. Curtis P. Rinsland
Mr. Gale A. Harvey

All at NASA Langley Research Center

C. Abstract of Research Objectives

Several NASA-funded atmospheric remote sensing experiments currently under development require extremely accurate knowledge of infrared spectroscopic line parameters (positions, intensities, assignments, halfwidths). The objective of this research task is to perform necessary laboratory measurements of such line parameters using tunable diode laser (TDL) systems, along with supplementary data obtained using Fourier-transform interferometers. This research focuses on two areas where the high resolution and radiometric accuracy of TDL systems are especially applicable: (1) Measurement of line positions and intensities for molecules with dense, complex spectra (e.g., nitric acid, ozone) where individual absorption lines usually cannot be resolved by other spectroscopic methods; (2) measurement of air-broadened or nitrogen-broadend halfwidths and their temperature dependence for atmospheric species whose infrared spectra are otherwise well known (e.g., ozone, methane).

D. Summary of Progress and Results

Since this is a new research effort which was not funded until the second half of F.Y. 1983, accomplishments have been rather limited. Detailed plans and preparations have been made for laboratory experiments to measure heavy isotopic ozone line positions and intensities in the 10 µm spectral region. Preliminary planning was also begun for measurements of ozone line intensities near 5.7 µm.

E. Journal Publications

None

Infrared Laboratory Measurements of
Stratospheric Constituents

Arthur G. Maki
Molecular Spectroscopy Division, 545
National Bureau of Standards
Washington, D.C. 20234

Research Objectives

In support of the upper atmospheric measurements programs involving infrared measurements from spacecraft, aircraft, and balloon flights as well as ground based measurements, this project uses high resolution infrared spectra to provide reliable parameters needed to measure the distribution of molecular species of particular interest for understanding the dynamics of atmospheric chemistry. The primary emphasis of this work is on species involved in the halogen (ClO_x) and nitrogen oxide (NO_x and HNO_x) chemistry cycles. Using techniques, software, and instrumentation developed in this laboratory in recent years, this project measures spectroscopic parameters (ro-vibrational constants, intensities, and pressure broadening constants) needed to model the spectroscopic properties of molecular species involved in the chemistry of the upper atmosphere. This data is made available to other workers in the form of molecular parameters as well as in the form of tabulated transition data calculated from the molecular parameters.

Summary of Progress and Results

The analysis of the spectrum of HNO_3 in the 850-950 cm^{-1} region has reached the point where we now know qualitatively what energy levels are perturbed and why. In the coming year we plan to develop a computer program that will allow us to quantitatively account for this perturbation in order to obtain a more complete assignment for the major absorption lines in the entire 850-950 cm^{-1} region.

Diode laser spectra of the ν_3 band of trans-HONO at 1263 cm^{-1} have been measured and analyzed. A paper is being prepared describing this work.

Our laboratory has recently acquired a BOMEM FTS spectrometer with a resolution of 0.003 cm^{-1}. This instrument greatly expands our capability for making high resolution measurements thoughout the entire infrared region.

Using Alan Pine's difference-frequency laser spectrometer we have begun studies of the line shapes of NO in the important pressure range of 0-100 Torr. Of particular interest is the degree to which collisional narrowing may affect the line shapes. This work will include measurements at room temperature and at reduced temperatures.

Some of our effort has been directed at providing improved frequency calibration standards so that certain field measurements can be more reliably tied to laboratory measurements. Part of this calibration effort involves a collaboration with Joe Wells and others at the NBS Laboratory in Boulder, Colorado. A particularly important result has been the accurate frequency measurement of the lines of the 2-0 band of CO. This band and the 1-0 band have been the traditional calibration standards to which most of the high resolution measurements are tied, especially measurements made with grating spectrometers. New frequency measurements using sub-Doppler techniques have shown that the generally accepted frequencies for the CO lines are too high by as much as 14 MHz. New frequency measurements have also been made on N_2O from 4340 to 4755 cm^{-1}. Calibration in the 1630 to 1950 cm^{-1} region has also been improved by making new frequency measurements on DBr. In the near future we hope to be able to apply these new frequency data to improve the frequencies of the 1-0 band of NO.

In another collaboration with J. Kauppinen at the University of Oulu (Finland), we are using carefully calibrated FTS spectra to improve the frequency calibration of the CO_2, N_2O, and OCS bands in the wavenumber interval from 480 cm^{-1} to 700 cm^{-1}.

Recent Publications

1. "Infrared Frequency Measurements on the ClO Fundamental Band," A. G. Maki, F. J. Lovas, and W. B. Olson, J. Mol. Spectrosc. 92, 410-418 (1982).

2. "Infrared Absorption Intensities of Nitrous Acid (HONO) Fundamental Bands," R. H. Kagann and A. G. Maki, J. Quant. Spectrosc. Radiat. Transfer, 30, 37-44 (1983).

3. "Diode Laser Spectra of Cis-HONO Near 850 cm^{-1} and trans-HONO Near 1700 cm^{-1}," A. G. Maki and R. L. Sams, J. Mol. Struct. 100, 215-221 (1983).

4. "Heterodyne Frequency Measurements of Carbonyl Sulfide Transitions at 26 and 51 THz. Improved OCS, $O^{13}CS$, and $OC^{34}S$ Molecular Constants," J. S. Wells, F. R. Petersen, and A. G. Maki, J. Mol. Spectrosc. 98, 404-412 (1983).

5. "Absolute Frequency Measurements of the 2-0 Band of CO at 2.3 μm; Calibration Standard Frequencies from High Resolution Color Center Laser Spectroscopy," C. R. Pollock, F. R. Petersen, D. A. Jennings, J. S. Wells, and A. G. Maki, J. Mol. Spectrosc. 99, 357-368 (1983).

6. "Infrared Absorption Intensities for N_2O_3," R. H. Kagann and A. G. Maki, J. Quant. Spectrosc. Radiat. Transfer, (in press).

1982-83 Research Summary--NASA Grant NSG 7473

A. Title of Research Task:

Laboratory Determination of Infrared Absorption Line Parameters for Molecules of Importance in Upper Atmospheric Research.

B. Principal Investigator: Professor Robert H. Hunt
Department of Physics
Florida State University
Tallahassee, Florida 32306

C. Research Objective:

The objective of this research is to obtain high-resolution laboratory measurements of the strengths, widths, and spectral positions of molecular infrared absorption lines for use in the interpretation of atmospheric spectra. The approach taken is to measure line strengths and make quantum number assignments for entire bands of atmospheric absorbers so as to obtain a complete knowledge of both the strengths and their temperature dependence. To obtain data at the best possible resolution, a Fourier transform spectrometer is being constructed to replace the present grating instrument.

D. Progress and Results:

The final results for absorption line assignments and intensities for several of the bands of methane studied in the 2600 to 3200 cm^{-1} region were published in 1982. Two new projects begun in 1981 continue as the major effort for 1982-83. The first of these has as its objective analysis of the vapor spectrum of hydrogen peroxide in the three micron region with resultant accurate determination of the ground state torsion-rotation levels of the molecule. Extensive spectra have been obtained with the Florida State University grating spectrometer and the Fourier transform spectrometer at the Kitt Peak solar telescope. Progress to date includes complete assignments to the torsion split antisymmetric stretching fundamental band and partial assignments to associated strong "hot-bands" of that vibration as well as to the moderate strength symmetric stretch fundamental.

The second project entails construction of a 0.0025 cm^{-1} resolution Fourier transform spectrometer at the Florida State University. Progress to date includes completion of construction on essentially all electronic and mechanical components with assembly and alignment underway.

E. Journal Publications

1. Molecular Constants for the Interacting Upper States of the ν_1, ν_3, $2\nu_2$, $\nu_2 + \nu_2$ and $2\nu_4$ Bands of Methane, J.E. Lolck, A.G. Robiette, L.R. Brown, and R.H. Hunt, J. Mol. Spectrosc. 92, 246-256 (1982).

2. Measurement and Analysis of the Infrared Absorption Spectrum of the $2\nu_2$ Band of Methane, R.H. Hunt, L.R. Brown, J.E. Lolck and A.G. Robiette, J. Mol. Spectrosc. 92, 246-256 (1982).

3. Analysis of the ν, and $\nu_2 + \nu_4$ Bands of Methane, L.R. Brown, R.A. Toth, A.G. Robiette, J.E. Lolck, R.H. Hunt and J.W. Brault, J. Mol. Spectrosc. 93, 317-350 (1982).

4. In addition, an abstract by W.B. Olson and R.H. Hunt on the analysis of the ground state of hydrogen Peroxide has been submitted to the 1983 Ohio State Symposium on Molecular Spectroscopy.

Title: Infrared Spectroscopic Investigations of Gases To Support Stratospheric Studies

Investigator: John H. Shaw The Ohio State University
Columbus, Ohio 43210

Research Objectives

The major emphasis of this program is to improve our knowledge of the absorption characteristics of the principal infrared absorbing gases in the atmosphere including CO_2, N_2O and O_3, to explore methods of simultaneous analysis of large quantities of spectral data to obtain the intensities and the widths of lines as functions of pressure and temperature, and to determine the spectroscopic factors which limit the accuracy and resolution of vertical profiles of atmospheric parameters inferred from measurement of atmospheric spectra.

Summary of Progress and Results for 1982 and 1983

The intensities, positions, and room temperature, self-broadened widths of lines of bands of CO_2 near 4 μm have been determined. Similarly, the nitrogen, oxygen, and air broadened widths and relative intensities of lines in N_2O bands near 4 μm have been measured by analyzing spectra obtained with a Fourier Transform spectrometer having a spectral resolution of about 0.07 cm^{-1}. During these studies the importance of modelling accurately a number of instrumental effects on the spectra were identified. These included uncorrected phase error, the effects of finite mirror retardation, finite detector size, background variations, and various apodization effects. These fitting methods have been described in detail in dissertations by Hoke and Hawkins.

Additional spectra of samples of N_2O and CO_2 broadened by nitrogen, oxygen and air at temperatures between 230 and 300 K have been collected and are being analyzed to determine the nature of the temperature dependence of the line widths. Self-consistent results have been obtained but additional laboratory measurements at higher temperature are expected to improve the precision of the results significantly.

Many investigators have determined the vertical mixing-ratio profiles of trace gases from solar occultation spectra. These analyses require the appropriate absorption parameters of the molecules of interest and a knowledge of the geometry of the optical path and the nature of the atmosphere traversed. By making some simplifying assumptions, estimates of the optimum relations between the uncertainty and resolution in these profiles when no a priori assumptions about the distribution of the absorbing gas are included have been determined and semiempirical relationships developed based on computer simulations. Similar studies of the factors influencing the accuracy of the molecular parameters obtained from laboratory spectra are being made. These are useful in developing appropriate methods of data analysis.

Journal Publications

M. L. Hoke and J. H. Shaw, "Analyses of CO_2 bands near 2600 cm^{-1}," Applied Optics, 21, 929 (1982).

M. L. Hoke and J. H. Shaw "Rotational Analysis of CO_2 bands near 4 μm Applied Optics, 21, 935 (1982).

R. L. Hawkins, M. L. Hoke and J. H. Shaw "Wavenumber Calibration of Fourier Transform Spectra," Applied Spectroscopy 37, 134 (1983).

M. L. Hoke and J. H. Shaw, "Parameters of CO_2 Bands near 3.6 μm," Applied Optics 22, 328 (1983).

R. L. Hawkins and J. H. Shaw, "Nitrogen, Oxygen, and Air-Broadened Widths and Relative Intensities of N_2O Lines near 2450 cm^{-1}," JQSRT 29, 543 (1983).

W. A. Shaffer and J. H. Shaw, "The Resolution and Vertical Mixing-Ratio Profiles of Atmospheric Constituents Retrieved from Solar Spectra", Submitted to Applied Optics.

A. Title of Research Task

Diode Laser Spectrum of Nitric Acid at 5.9 Micrometers and Carbonyl Sulfide Frequency/Wavelength Standards for Calibration of Nitric Acid Bands Both at 5.9 and 11.4 Micrometers.

B. Investigators and Institution

J. S. Wells, F. R. Petersen (principal investigators),
D. A. Jennings and C. R. Pollock*
Time and Frequency Division
Boulder, Colorado 80303

A. G. Maki
Molecular Spectroscopy Division
National Bureau of Standards
Washington, DC 20234

*NRC post doctoral fellow, now at Cornell University

C. Abstract of Research Objectives

Spectroscopic techniques are becoming even more widely used to monitor concentrations of minor atmospheric constituents (of particular interest are those placed there by man) and their possible role in altering the atmosphere. The broad objectives of this work are to provide frequency/wavelength standards for the calibration of the spectra of these constituents. Once the frequency calibration tables are completed, they are sometimes used to make high resolution measurements on molecules of high interest, such as HNO_3.

D. Summary of Progress and Results

A $^{12}C^{16}O_2$ laser has been stabilized to the 01^11-$[11^10,03^10]_I$ hot band features and the transition frequencies measured [1] with the CO_2 laser synthesizer. These hot band features form an additional synthesis basis which further expands capabilities.

A tunable diode laser and CO_2 laser synthesizer were used to measure hot band features of some isotopic variants of OCS at 26 THz, and some 2 ν_1 bands of OCS, $O^{13}CS$ and $OC^{34}S$ at 5I THz. [2] These measurements were the first we have made using the CO laser as a transfer oscillator. These measurements were completed in time to appear in the OCS Frequency Calibration Atlas. [3] This Atlas covers the regions of the mid infrared: 815-892 cm^{-1}, 1008-1092 cm^{-1}, 1649-1738 cm^{-1}, 1850-1921 cm^{-1} and 2013-2140 cm^{-1}. Uncertanties range from 1 MHz in best cases to up to 10 MHz. Spacing and relative intensities of hot band and isotopic species permit unambiguous line identification. The Atlas contains 6600 entries. The CO laser was also used as an auxiliary oscillator to transfer CO_2 laser standard frequencies in measurements of deuterium bromide. DBr covers the range 1630-1980 cm^{-1} and thus fills some gaps in OCS coverage. The DBr calibration table [4] has uncertainties of 3 MHz or less for both $D^{79}Br$ and $D^{81}Br$ over most of the region indicated.

Reference frequencies from the OCS calibration atlas were used to calibrate the ν_5 band of HNO_3. Detailed experimental spectra in the 862-872 cm^{-1} were turnished to A. Goldman of Denver University to assist him in his balloon experiments. Further work resulted in coverage of most of the P Branch. Those results were combined with Maki's NBS Gaithersburg measurements, analyzed and published in J. Mol. Spectrosc. [5] Itensity measurements have also been made on selected features in this band. The heterodyne system was used to measure the TDL linewidth in these measurements. [6]

Tunable laser - CO_2 laser synthesizer coverage has been extended to the 4000-5000 cm^{-1} region where NASA resources were expended for color center laser development. The color center laser was later used to measure frequencies in the 2-0 band of CO. Very accurate saturated absorption frequency measurements were possible and the band center is now determined to better than 0.1 MHz. The new band center is about 14 MHz lower than Guelachvilli's results in 1976. A new calibration table has been published. [7] Subsequent Doppler limited measurements on the 00^02-00^00, 20^01-00^00 and 12^01-00^00 bands of N_2O [8] now (along with the CO work) provide coverage over most of the 4100-4800 cm^{-1} region. The current status of calibration molecules was reviewed at SPIE. [9]

E. Journal Publications

1. "Heterodyne Frequency Measurements and Analysis of $^{12}C^{16}O_2$ Laser Hot Band Transitions," F. R. Petersen, J. S. Wells, K. J. Siemsen, A. M. Robinson and A. G. Maki, J. Mol. Spectrosc. (in press).

2. "Heterodyne Frequency Measurements of Carbonyl Sulfide Transitions at 26 and 51 THz; Improved OCS, $O^{13}CS$ and $OC^{34}S$ Molecular Constants," J. S. Wells, F. R. Petersen and A. G. Maki, J. Mol. Spectrosc. 98, 404-412 (1983).

3. "Tables of Carbonyl Sulfide (OCS) Absorption Line Frequencies and Wavenumbers for the Calibration of Tunable Infrared Laser," A. G. Maki. J. S. Wells, F. R. Petersen, W. J. Lafferty, W. B. Olson, A. Fayt, and J. P. Sattler, J. Phys. Chem. Ref. Data, (1983).

4. "Improved Deuterium Bromide 1-0 Band Molecular Constants from Heterodyne Frequency Measurements," F. R. Petersen, J. S. Wells and A. G. Maki, J. Mol. Spectrosc. (in press).

5. "High Resolution Spectrum of the ν_5 Band of Nitric Acid (HNO_3) Near 880 cm^{-1}," A. G. Maki and J. S. Wells, J. Mol. Spectrosc. (in press).

6. "Intensity Measurements of the ν_5 Band of HNO_3 with a Tunable Diode Laser, A. G. Maki, J. S. Wells, F. R. Petersen, D. J. Sukle and P. S. Connell, J. Mol. Spectrosc. (in process).

7. "Absolute Frequency Measurements of the 2-0 Band of CO at 2.3 μm, Calibration Standard Frequencies From a Color Center Laser Spectroscopy," C. R. Pollock, F. R. Petersen, D. A. Jennings, J. S. Wells and A. G. Maki, J. Mol. Spectros. 99, 357-368 (1983).

8. "Absolute Frequency Measurements of the 00^02-00^00, 20^01-00^00, and 12^01-00^00 Bands of N_2O by Heterodyne Spectroscopy," C. R. Pollock, F. R. Petersen, D. A. Jennings, J. S. Wells and A. G. Maki, J. Mol. Spectrosc. (in process).

9. "Heterodyne Frequency Measurements and Frequency Calibration Standards for Tunable Diode Lasers," J. S. Wells, F. R. Petersen, and A. G. Maki, SPIE Proceedings, 438 9 p. (1983).

A. TITLE OF RESEARCH TASK

MILLIMETER AND SUBMILLIMETER SPECTROSCOPY OF MOLECULES OF ATMOSPHERIC IMPORTANCE

B. INVESTIGATORS

Frank C. De Lucia
Department of Physics
Duke University
Durham, North Carolina 27706

Paul Helminger
Department of Physics
University of South Alabama
Mobile, Alabama 36688

C. ABSTRACT OF RESEARCH OBJECTIVES

The goal of this work is to provide millimeter and submillimeter spectral maps of atmospheric molecular species either by direct measurement or well founded calculation. This work supplies a basis for the selection of transitions as candidates for field monitoring systems as well as substantial information about potential coincidences with interfering lines. Emphasis is placed on detailed analyses of large data sets both because the special spectroscopic complexities of some of the species require it for surity of assignment, and also because the results provide valuable information to workers in other spectral regions.

D. SUMMARY OF PROGRESS AND RESULTS

It is the goal of our work to provide a "complete" spectroscopic analysis of a substantial data base. For most of the light molecules of atmospheric importance, this requires the broad spectral coverage of the millimeter and submillimeter spectroscopic techniques that we have developed. The extensive analysis that result from this work not only provide for current needs, but also future, as yet unanticipated requirements. They also provide information that is broadly applicable to work in other spectral regions, especially the infrared.

HO_2: HO_2 is an unstable molecular species which is spectroscopically complex because it is a light asymmetric rotor with unpaired electronic spin and nuclear hyperfine structure. We have completed a detailed analysis of this species which is based on measurement of over 100 previously unobserved transitions.

NO_2: NO_2 is also a light asymmetric rotor with unpaired electronic spin and nuclear hyperfine structure. However, because the relative sizes of rotational energy, spin rotation energy, and nuclear hyperfine energy are different than those in HO_2, we had to develop a different analytical approach for our model building. In this work we observed 425 new lines of $^{14}N^{16}O_2$ in the spectral region between 100 and 600 GHz.

CF_2: CF_2 is a light asymmetric rotor with no additional spectroscopic complications. In this work, 62 new millimeter and submillimeter transitions were observed and a wide ranging spectral map produced.

HNO: HNO is an unstable molecular species with a rather sparse millimeter and submillimeter spectrum. In this work, we have measured and analyzed approximately 50 new millimeter and submillimeter lines.

We have also made extensive new measurements in the 500-1100 GHz spectral region. For many species, this is the region of maximum sensitivity for remote sensing experiments based upon rotational spectra. This work includes studies of HOOH, HNO_3, H_2O, and HDO. Our earlier work on these species has been used extensively by the atmospheric community for many diverse purposes. These include interpretations of field observations, aid in the assignment and analysis of infrared studies, and the testing of theoretical models.

HOOH: Hydrogen peroxide is a light asymmetric rotor with internal rotation. As such, it has an extremely complicated spectrum with substantial theoretical complexity. In our earlier work, we demonstrated a simple theoretical approach that has been widely adopted. Our new measurements provide extension of this work from around 600 GHz to the THz region.

HNO_3: Nitric Acid is an asymmetric rotor with a strong, dense spectrum. Our earlier work contained extensive measurements through about 550 GHz and provided a spectral map for the regions of current field measurements. This new work substantially extends the spectral region.

Water: We have had a long standing interest in water both because of its importance to many atmospheric problems and because it is a testing ground for centrifugal distortion theory. As a result, we have made extensive new measurements, primarily in the 500-1100 GHz region, on the major isotopes, H_2O, HDO, and D_2O of this fundamental species. We have also completed new analyses of these data. This work also makes a significant contribution to infrared studies by providing extensive amounts of very high accuracy information about the ground vibrational state energy level structure.

E. JOURNAL PUBLICATIONS

1. "The Millimeter and Submillimeter Spectrum of HO_2: The Effects of Unpaired Electronic Spin in a Light Asymmetric Rotor," Arthur Charo and Frank C. De Lucia. J. Mol. Spectrosc. 94, 426-436 (1982).

2. "The Millimeter and Submillimeter Spectrum of NO_2: A Study of Electronic Effects in a Nonsinglet Light Asymmetric Rotor," Wayne C. Bowman and Frank C. De Lucia, J. Chem. Phys. 77, 92-107 (1982).

3. "The Millimeter and Submillimeter Spectrum of CF_2 and Its Production in a dc Glow Discharge," Arthur Charo and Frank C. De Lucia, J. Mol. Spectrosc. 94, 363-368 (1982).

A. Measurements of Quantitative Infrared Line Strength Parameters for the HO_2 Radical

B. Mark S. Zahniser and Alan C. Stanton
Aerodyne Research, Inc.
45 Manning Road, Billerica, MA 01821

C. Research Objectives

The HO_2 radical is an important trace constituent of both the troposphere and the stratosphere. Determinations of its atmospheric concentration and studies of its reaction rates and mechanisms are necessary for understanding the chemistry of stratospheric ozone. This research program will determine absolute infrared line absorption coefficients and lineshape parameters for the vibrational bands of HO_2 using high resolution tunable diode laser spectroscopy. This information will be useful for in situ and remote measurements of HO_2 in the atmosphere and will also provide a method for directly detecting HO_2 in laboratory kinetic studies.

D. Summary of Progress and Results

The HO_2 radicals generated in a discharge-flow system have been observed with tunable diode laser absorption in the P-branch of the ν_3 vibrational band at 1080 cm^{-1}. The observed line positions agree within 2 to 5 x 10^{-3} cm^{-1} with those calculated from the molecular constants for the ν_3 band obtained from a previous study using laser magnetic resonance spectroscopy. The band strength has been determined by observing line center absorptions when HO_2 is produced in the reaction $F + H_2O_2 \rightarrow HO_2 + HF$ (k_1) with a measured concentration of atomic fluorine and excess hydrogen peroxide. F-atom concentrations are measured by diode laser absorption of the spin-orbit transition at 404 cm^{-1}.

The analysis accounts for HO_2 losses due to the reactions of $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (k_3) and $F + HO_2 \rightarrow HF + O_2$ (k_4). The experimental data are consistent with a value of $k_3 = (1.6 \pm 0.3) \times 10^{-12}$ cm^3s^{-1} and a ratio $k_4/k_1 = 1.0 \pm 0.4$. The line strength for the $6_{15} \leftarrow 7_{16}$ F_1 transition is 2.9×10^{-21} cm^2 $molecule^{-1}$ cm^{-1} which corresponds to a ν_3 band strength of 34 ± 9 cm^{-2} $(STP\ atm)^{-1}$. This value is a factor of 6 lower than previous ab initio calculations. These results will be useful in assessing the feasibility of atmospheric measurements of HO_2 using infrared absorption techniques.

E. Publications

"A Measurement of the ν_3 Vibrational Band Strength of the HO_2 Radical", Mark S. Zahniser and Alan C. Stanton, Chemical Physics Letters, to be published (1983).

SUMMARY OF RESEARCH

Title: A Reassesment of the Predissociation Linewidths in the Schumann-Runge Bands of O_2

Investigator: Paul S. Julienne
Molecular Spectroscopy Division
National Bureau of Standards
B268 Physics Building
Washington, D.C. 20234

Abstract of Ojectives:

The absorption of solar ultraviolet radiation by the Schumann-Runge bands of O_2 controls the transmission of the solar flux in the 200-175 nm range through the upper stratosphere and is a process of fundamental importance to stratospheric photochemistry. Construction of an accurate solar transmission model has been hampered by experimental uncertainties in the oscillator strengths and predissociation linewidths of these bands. The goal of the present research is to construct a reliable predictive theoretical model for the individual predissociation linewidths for the vibrational-rotational fine structure components for all the isotopic combinations of O_2. This represents an extension of previous calculations by the principal investigator. The work is divided into three tasks. (1) Use a new accurate ab initio technique to recalculate the spin-orbit matrix elements coupling the $B^3\Sigma_u^-$ state to the four $^5\Pi_u$, $^3\Sigma_u^+$, $^1\Pi_u$, and $^3\Pi_u$ predissociating states. (2) Reassess the roles of these states in the predissociation and calculate the dependence of linewidth on rotational and fine structure quantum numbers. (3) Predict the linewidths for isotopic species containing ^{16}O, ^{17}O, and ^{18}O.

Summary of Progress

This research requires 0.25 man-year during the interval March 1983 - February 1984. Our initial prelimary work has been to lay out a strategy for carrying out the ab initio calculations needed to calculate the spin-orbit matrix elements. Carrying out the actual calculations is planned for October-December 1983, with approximately one month allocated to each of the three tasks.

Biennial Report on NASA Upper-Atmospheric Research Program

Research Task: Line Parameters for the Fundamental Bands of HCl and HF

Investigator and Institution:

Dr. Alan S. Pine
Molecular Spectroscopy Division
National Bureau of Standards
B268 Physics Building
Washington, D.C. 20234

Objectives:

The purpose of this program is to provide a laboratory data base in support of the NASA Halogen Occultation Experiment (HALOE) which is designed to obtain measurements of key constituents in the ClO_x, NO_x, and HO_x cycles that affect the ozone balance in the upper atmosphere. In particular the HALOE project will be monitoring the HCl and HF molecular channels using nondispersive spectral correlation techniques. These techniques require accurate laboratory measurements of the line and band intensities of the fundamental vibrations of HCl and HF, as well as detailed knowledge of their polymerization and of their self- and atmospheric-pressure-broadened linewidths and shifts. The self-broadening parameters and polymerization properties are required to characterize the relatively high-pressure sample gas correlation cells to be flown by NASA. The laboratory spectroscopy of the HCl and HF intensities, widths and polymers will be carried out with a very high resolution tunable difference-frequency laser recently constructed at NBS for precision infrared measurements in the 2.2 to 4.2 μm spectral region.

Summary of Progress:

The precision measurement of line intensities, pressure-broadened linewidths and polymerization of HCl and HF in support of the NASA Project HALOE upper-atmospheric monitoring program requires both a very high-resolution, high-sensitivity spectrometer and a stable, reliable, reproducible sample handling procedure. The spectrometer to be used is a tunable difference-frequency laser designed to operate in the 2.2 to 4.2 μm infrared region by mixing of single frequency argon ion and tunable dye laser radiations in a $LiNbO_3$ nonlinear optical crystal. This difference-frequency laser has been recently constructed at NBS with improved servo-controls which yield an instrumental linewidth of ∿ 1 MHz, linear scan control to better than 0.1%, signal-to-noise ratio ∿ 1000:1, and digital data acquisition and processing. The Doppler widths of these molecules are ∿ 330 MHz for HF and ∿ 180 MHz for HCl; so the instrumental distortion of the line profiles is negligible, yielding very trustworthy spectral measurements. The difference-frequency laser system has been tested throughout the spectral range required for HF and HCl and some quite interesting preliminary observations have been made of the dimers of these molecules.

At present we are concentrating our efforts on the sample handling techniques. Both HF and HCl are extremely reactive vapors and require special materials in sample cell construction and pressure gauges in order to make reliable quantitative measurements. Special cells have been designed using inert Monel construction and valves with sapphire and CaF_2 windows and Teflon gaskets to minimize wall adsorption and desorption and chemical contamination. A variety of different path length cells are required (between 1 mm and 1 m) for the self- and atmospheric-broadening measurements in order to avoid saturation of the infrared absorption. Distillation and chemical processing of the gases are required to eliminate impurities in the commercially available samples. Precision pressure measurements will be made using cross-calibrated capacitance manometers of inert construction.

SRI International

ENERGY TRANSFER EFFECTS IN LASER FLUORESCENCE MEASUREMENT OF ATMOSPHERIC OH

Richard A. Copeland and
David R. Crosley

SRI International
Molecular Physics Laboratory
Menlo Park, California 94025

Objectives

The OH radical is directly involved in numerous important chemical processes throughout the atmosphere. Catalytic ozone destruction in the stratosphere, conversion of CO to CO_2, and photochemical smog formation are processes where better knowledge of OH radical concentrations may provide mechanistic insight. Accordingly, the development of the laser-induced fluorescence (LIF) technique to measure atmospheric OH has received much experimental emphasis. One serious limitation of this technique to date is the requirement of detailed and accurate information on collisional behavior of the $A^2\Sigma^+$ electronic state, which is essential for correct data interpretation. Even though studied by several workers, significant disagreements and inconsistencies exist in many of the important rate constants while others remain undetermined. This report describes the steps taken in the past year to obtain the necessary accurate energy transfer data for of modeling collisional effects on the OH monitoring LIF experiments.

MP83-159
09/14/83

SRI International

333 Ravenswood Ave. • Menlo Park, CA 94025
(415) 326-6200 • TWX: 910-373-2046 • Telex: 334-486

Summary of Progress and Results

The experimental apparatus assembled for this LIF study consists of a two-stage flow cell, similar in design to that of McDermid and Laudenslager,[1] to produce the OH and introduce quenching gases, a laser to excite the molecules from the ground to the first electronic state and the detection system to monitor the fluorescence and record the data. A computer interface in conjuction with a data analysis program specifically designed to accommodate the OH laser-induced fluorescence data, permits the handling of the large quantity of experimental observations needed on the project. Using this apparatus, we have begun to measure both radiative lifetimes and electronic quenching rates in the v'=0 rotational manifold of the $A^2\Sigma^+$ state. We have obtained the following preliminary results:

- Collision-free radiative lifetimes, directly measured for several rotational levels in v'=0 (for example, N'=0, J'=1/2 is 676 ± 10 nsec and N'=4, J'=9/2 is 694 ± 10 nsec), agree well with those of German[2] and Dimpfl and Kinseys[3] but are slightly lower than those of McDermid and Laudenslager.[1]

- Electronic quenching of OH (v'=0) by N_2 decreases as the rotational energy of the OH increases (from $4.9 \pm 0.6 \times 10^{-10}$ cm^3 sec for N'=0 to $3.0 \pm 0.6 \times 10^{-10}$ cm^3 for N'=4 to $1.5 \pm 1.0 \times 10^{-10}$ cm^3 sec for N'=7), supporting a similar observation by McDermid and Laudenslager.[1]

- Electronic quenching of OH (v'=0) by O_2 and H_2O decreases as the rotational energy of the OH increases from N'=0 to N'=5 by 35% and 15% respectively.

These experimental results are presently being incorporated into a computer model of the OH relaxation which later will be used for simulating the monitoring experiments.

1. I. S. McDermid and J. B. Laudenslager, J. Chem. Phys. 76, 1824 (1982).
2. K. R. German, J. Chem. Phys. 62, 2584 (1975).
3. W.L. Dimpfl and J. L. Kinsey, JQSRT 21, 233 (1979).

Publication

Partially supported on this project was the preparation of the invited review article:

D. R. Crosley and G. P. Smith, "Laser-Induced Fluorescence Spectroscopy in Combusion Diagnostics," Opt. Engr., in press (September 1983).

and the invited review presentation:

D. R. Crosley , "Laser-Induced Fluorescence for Combustion Chemistry," American Physical Society Meeting, San Francisco, California, November 1983.

Fully supported by this project is the contributed paper:

R. A. Copeland and D. R. Crosley, "Rotational Level Dependence of Electronic Quenching in OH ($A^2\Sigma^+$, v'=0)," American Physical Society Meeting, San Francisco, California, November 1983.

III. THEORETICAL STUDIES

A. ONE DIMENSIONAL AND TWO DIMENSIONAL MODELS

B. THREE DIMENSIONAL MODELS

C. MOLECULAR CALCULATIONS

A. ONE DIMENSIONAL AND TWO DIMENSIONAL MODELS

NASA - Ames Research Center

Summary of NASA-sponsored Upper Atmospheric Research under Research Task entitled:

A. A Method for Evaluating the Transports by Mean and Deviatory Motions in a Two-Dimensional Model.

B. Research is an extension of FAA contract initiated by Prof. E. F. Danielsen while at Oregon State University. After joining NASA Ames Research Center in the Fall of 1979, Dr. Danielsen continued the research with the cooperation of Prof. C. Riegel and two research associates -- R. S. Hipskind and S. Gaines of San Jose State University. Recently, with the death of Prof. Riegel, the two associates have joined Informatics and the work is continuing with Dr. Danielsen as principal investigator and R. S. Hipskind and S. Gaines as assistants under contract with Informatics.

C. Objectives

The primary objective under the FAA sponsorship was to develop and test an objective method for determining the components of a generalized transport tensor for two-dimensional chemical-photochemical models of the stratosphere. After the tensor evaluation method was completed the primary objective became: To generate a uniformly distributed set of dynamically balanced meteorological variables from the nonuniformly distributed radiosonde, aircraft and satellite measurements to which the tensor evaluation method could be applied. The objective, numerical analysis and diagnostic methods being developed have been utilized, also, to support NASA-sponsored aircraft and balloon experiments which in turn provide direct evidence of stratospheric transport processes and stratospheric-tropospheric exchange processes described statistically by the transport tensor.

D. Summary of Progress and Results

Following publication of the tensor evaluation method in the July 1981 Journal of Atmospheric Sciences, our research has focused on developing and testing objective, numerical analysis and diagnostic methods. The diagnostic is based on an iterative solution of the vorticity and divergence (balance) equations in isentropic coordinates to take advantage of the adiabatic approximation. This method yields a stream function and velocity potential from which the ageostrophic velocities including the adiabatic vertical velocities are derived plus the Montgomery stream function from which the geostrophic velocities and the static stability are derived. The method is diagnostic rather than predictive to determine a balanced set of variables representative of the large scale atmospheric conditions.

To date, all state-of-the-art analysis techniques have been tested and none have proven to be satisfactory for global analyses of synoptic data. The difficulty with statistical methods, including sophisticated multivariant methods with minimization of the sum of weighted squares of respective deviations, is the necessary assumption of isotropy and homogeneity. Conversely, hand analyses which utilize pattern recognition and time-space continuity to resolve the anisotropy and asymmetries are too time consuming to be used operationally.

Despite these difficulties with synoptic analyses excellent results have been obtained for zonal-monthly mean analyses. An objective error detection method has been applied to derive monthly means and standard deviations from the radiosonde observations of all stations over the globe. Starting with zonal means of height, temperature, dew point depression and zonal wind velocity, a least squares analysis of the heights at mandatory pressure levels is obtained by expanding the heights and their latitudinal derivatives in Legendre polynomials and using the geostrophic wind approximation to relate the mean winds to their derivatives. Similarly, the mean virtual temperatures at constant pressure are analyzed using the vertical shears of the mean wind as a vectoral guide to the temperature gradients. Although analyzed independently at 16 levels from 1000 to 10 mbs the results are beautifully consistent, including hydrostatic tests, and require no latitudinal filtering. Vertical filtering is required only occasionally at latitudes south of 50 S, where large data gaps between the continents and Antarctica can produce nonrepresentative oscillations.

Eight years of data, 1973 through 1980, are now being processed and an Atlas will be prepared for distribution. These analyses will provide reliable information on the semiannual, annual and biannual variations as a function of latitude and pressure (or height or potential temperature). In addition, the latitudinal-height distribution of potential vorticity and its global mean values is computed for evaluating past, present and future correlations with trace gases and aerosols. This quasi-conservative scalar is of major importance to NASA's evaluation of remote satellite observations. Previously, only a few hand computed analyses were made over a limited latitudinal range.

E. Journal Publications

As discussed above, numerical analyses including latitudinal-height cross-sections drawn by computer for each of 96 months are now being generated for an Atlas and for a journal publication. No attempt was made to publish until the complete technique was developed and tested. In the meantime, two papers were published as a result of NASA's U-2 experiments to study tropospheric-stratospheric exchange in the tropics, and two more involving balloons in the extratropics (one with the U-2 aircraft) are in manuscript form. The publications are:

Danielsen, E. F., Statistics of cold cumulonimbus anvils based on enhanced infrared photographs, Geophys. Res. Lett., Vol. 9, No. 6, 601-604, 1982.

Danielsen, E. F., A dehydration mechanism for the stratosphere, Geophys. Res. Lett., Vol. 9, No. 6, 605-608, 1982.

Doherty, G. M., Newell, R. and Danielsen, E., Radiative heating rates near the stratospheric fountain, Accepted by J. Geophys. Res., August 1983.

Title:	Stratospheric Photochemistry and Composition
Principal Investigator:	R. S. Stolarski NASA/Goddard Space Flight Center Code 964 Greenbelt, MD 20771
Co-Investigators:	P. D. Guthrie C. H. Jackman NASA/Goddard Space Flight Center Code 964 Greenbelt, MD 20771

A two-dimensional photochemical model has been developed which uses fourth-order spatial differencing and the photochemical package developed by J. R. Herman. The primarily advective transport is determined by a diabatically driven circulation which should form a first approximation to actual atmospheric transport. Experiments have been carried out transporting the source gases N_2O, $CFC\ell_3$ and $CF_2C\ell_2$ with oxone held fixed at observed values. The results agree with data about as well as other models which have highly tuned transport. The major characteristic of the disagreement is a tendency for the model profiles at mid-latitudes ($\sim$45°) to be larger than measurements as if the tropical bulge in tracer contours extends to higher latitudes in the model than is reasonable. This discrepancy cannot be removed by diffusion terms and points to a need for reevaluation of the net heating which drives the diabatic circulation. Studies are also underway to expand to a full chemistry set in the model working toward a fully self-consistent calculation of ozone.

The 1D steady-state photochemical model, which has been used in the past for the study of uncertainty propagation in perturbation calculations, has been reactivated. The problem under examination is whether all of the chemistry changes due to improved reaction rates and new chemical pathways have significantly improved our perception of the chemical uncertainty in perturbation problems. Monte-Carlo runs were made for 200 cases varying rate coefficients randomly about their mean values for each of two rate coefficient data sets; the CIAP 1975 evaluation and the 1982 JPL Report of the NASA-CODATA evaluation. Results for NO_x injection at 20 km showed smaller uncertainties for the more recent data set primarily because the lower end of the probability distribution, i.e. the largest column ozone decreases, was truncated.

Publications:

1. Evidence for Quasi-Periodic Components in Dobson Network Total Ozone Records, P. D. Guthrie, J. Geophys. Res., 88, 3809-3818, 1983.

2. A Diabatic Circulation Experiment in a Two Dimensional Photochemical Model, P. D. Guthrie, C. H. Jackman, J. R. Herman, and C. J. McQuillan, submitted to J. Geophys. Res., 1983.

3. Sensitivity of N_2O, $CFC1_3$, and CF_2C1_2 Two Dimensional Distributions to O_2 Absorption Cross Sections, C. H. Jackman and P. D. Guthrie, to be submitted to J. Geophys. Res., 1983.

A. APPLICATION OF STRATOSPHERIC MODELLING TO DATA INTERPRETATION

B. Dr. Jay R. Herman and Ms. C. J. McQuillan
Code 964
Goddard Space Flight Center
Greenbelt, Md. 20771

C. Research Objectives

An improved treatment of uv radiative transfer is under development as part of a detailed stratospheric photochemistry (1-D and 2-D) modelling effort. The research is aimed towards the interpretation of uv spectral data obtained from recent balloon flights that show a larger scattered solar flux component than is currently calculated. The data is being used to guide the development of a sufficiently fast algorithm for use with 2-D, 3-D, and the Lagrangian parcel models that can accurately represent the low sun angle scattering effects typical of the polar regions. This same radiative transfer algorithm is being used in the time dependent 1-D photochemistry model to interpret constituent data obtained near sunrise and sunset where the scattered flux component can contribute significantly to the calculated densities. A major research objective is the development of a Lagrangian parcel model. Using a preliminary version of this model it has been shown that the ozone density calculations for parcels following low order wave number driven motions of the atmosphere are quite different from similar calculations based on the zonal mean flow.

D. Summary of progress and results.

The analysis of SABE 1 (Solar Atmospheric Balloon Experiment) and SABE 3 data has yielded several new results. Most important is the discovery of the large uv scattered flux component near 200 nm (Herman and Mentall, 1982a) and the new determination of the O2 Herzberg absorption cross section between 200 and 230 nm (Herman and Mentall, 1982b). Additional scattered flux data from SABE 3 and some recent balloon flights are being analysed. Preliminary results show that the large scattered flux component is a function of altitude and time of day.

The 1-D stratospheric photochemistry model has been used to predict the composition of non-methane hydrocarbons in the troposphere and lower stratosphere (Aikin et al., 1982). This work has been extended to include additional hydrocarbon chemistry and to explore its influence on the ozone concentration (Aikin et al., 1983). The 1-D time dependent version of the model is beimg used to investigate the seasonal dependence of the ozone concentration in the stratosphere and its relation to temperature variations. The results clearly show the regions where the observed seasonal ozone variations can be explained by photochemistry and where the atmospheric dynamics effects are likely to play an important role.

The Lagrangian parcel model has been developed to the point where it is possible to show that the concentrations of constituents whose chemical lifetimes are on the order of a day or longer are dependent on the detailed motions of an air parcel through the atmosphere. The most dramatic differences occur in the polar regions where the ozone concentrations in a parcel following the low order wave number driven motions can differ by 50 percent from that calculated in air parcels following the mean motion.

E. Journal Publications

Herman, J.R. and J.E. Mentall, The direct and scattered solar flux within the stratosphere, J. Geophys. Res., 1319-1330, 1982a.

Herman, J.R. and J.E. Mentall, 02 absorption cross sections (187-225nm) from stratospheric solar flux measurements, J. Geophys. Res., 87, 8967-8975, 1982b.

Aikin, A.C., J.R. Herman, E.J. Maier, and C.J. Mcquillan, Atmospheric chemistry of ethane and ethylene, J. Geophys. Res., 87 3105-3118, 1982.

Aikin, A.C., J.R. Herman, E.J. Maier, and C.J. Mcquillan, Stratospheric Distribution Peroxychloroformyl Nitrate, Submitted to Geophys. Res. Letters, 1983.

RESEARCH SUMMARY

NASA Grant NAGW-413

1982-83

California Institute of Technology
Pasadena, California 91125

Task I: Photochemical Modeling for Field Measurements

Investigators: Dr. Yuk L. Yung
Dr. Mark Allen
Dr. Lucien Froidevaux

Abstract of Research Objectives:

The general purpose of this research is to study various questions related to the radiation field and the chemistry in the Earth's upper atmosphere, and to stimulate further measurements in order to test the theory and help resolve existing discrepancies. Problems amenable to analysis via a one-dimensional photochemical model are emphasized. These include treatments of absorption and scattering of solar radiation (absorption in the Schumann Runge bands and Herzberg continuum of O_2, diffuse flux effects in a spherical shell atmosphere) and the resulting impact on the photochemistry and on trace species' vertical profiles, as well as studies of the partitioning of chlorine and fluorine source species and radicals diurnal variations, and the abundance of light and heavy ozone (see Task II).

Summary of Progress and Results

We have developed a one dimensional photochemical model of the Earth's stratosphere, in order to provide an up-to-date comparison with mid-latitude observations.

We briefly comment on the scattered solar flux measurements (at 40 km) by J.R. Herman and J.E. Mentall. A 10% ratio of scattered to direct flux at 20 nm is unexplainable, without the existence of an unknownn scattering component. We also explicitly demonstrate the first-order effects of the inclusion of the diffuse radiation in a spherical shell atmosphere, for solar zenith angles close to 90°. Changes in model concentrations are largest for short-lived radicals such as O, OH, ClO, and NO in the lower stratosphere, but relatively small compared to current observational uncertainties.

We propose that a significant overestimate of the molecular oxygen absorption cross section near 210 nm is in large part responsible for the discrepancy between observed and modeled vertical profiles of some halocarbons ($CFCl_3$ in particular).

Model ClO profiles now show much better agreement with mean data, due to certain kinetic rate constant revisions affecting the abundance of HO_x in the lower stratosphere. The diurnal vairation of ClO observed from the ground by P. Solomon and coworkers is consistent (to first order) with our diurnal model results and provides indirect evidence for the existence of $ClONO_2$. The main uncertainty relating to fluorine products concerns the value of the quantum yield for COF_2 photodissociation, which affects the predicted abundance of HF by up to 40% in the upper stratosphere. There is reasonable agreement between existing HO_x and NO_x observations and model results, although the observed scatter in certain abundances remains to be understood and key simultaneous observations have not been satisfactorily performed.

Publications

Allen, M., and J.E. Frederick, Effective photodissociation cross sections for molecular oxygen and nitric oxide in the Schumann-Runge bands, J. Atmos. Sci., **39**, 2066, 1982.

Froidevaux, L., and Y.L. Yung, Radiation and chemistry in the stratosphere: Sensitivity of O_2 absorption cross sections in the Herzberg continuum, Geophys. Res. Lett, **9**, 854, 1982.

Froidevaux, L., M. Allen and Y.L. Yung, manuscript in preparation, 1983.

Froidevaux, L., Ph.D. Thesis, Caltech, 1983.

SUMMARY OF RESEARCH TASK

A. Title: Theoretical Studies of the Atmosphere and Data Analysis

B. Investigators and Institutions:

Principal Investigator: Linwood B. Callis
NASA Langley Research Center
Hampton, VA 23665

Co-Investigators: Robert E. Boughner
Kenneth V. Haggard
NASA Langley Research Center
Hampton, VA 23665

Murali Natarajan
Systems and Applied Sciences Corporation
NASA Langley Research Center
Hampton, VA 23665

C. Abstract of Research Objectives: The objectives of the present research are to conduct scientific investigations directed toward the development of a better understanding of the photochemistry, transport, and thermal effects in the natural and perturbed stratosphere. Studies are conducted utilizing existing photochemical models, radiative codes (solar, infrared, radiative-convective), trajectory packages, and software developed and used for the analysis of satellite data. Emphasis during these studies is on the use of models in conjunction with available data (especially LIMS data). Efforts in the present research program are directed to: (1) Studies of stratospheric odd nitrogen; (2) general photochemical consistency studies; (3) thermal balance and photochemical effects of elevated levels of trace gas concentrations (CO_2, CH_4, N_2O, and CFM's); and the interaction between photochemical and transport effects in establishing the stratospheric thermal and trace species climatology.

D. Summary of Progress and Results: During 1982 and 1983 (to date), the following tasks have been accomplished:

(i) Used photochemical models, trajectory analysis, and LIMS data to explain the mechanism which forms and sustains the presence of exceedingly sharp gradients in column NO_2 ("Noxon Cliff") in the Northern Hemisphere wintertime. The explanation of this phenomenon was given a high priority by a National Research Council report. The first presentation of these results was given in Boston in March 1983 at an AMS meeting. A paper describing this study is currently in press (GRL).

(ii) Conducted first fully self-consistent studies of the thermal and photochemical effects in the troposphere and stratosphere of increased atmospheric levels of trace constituents such as CO_2, CH_4, N_2O, CO, and CFM's. In addition to stratospheric ozone decreases, this study identified and discussed significant tropospheric ozone perturbations as much as 16 percent reduction for a 2 x CO_2 + CFM case. Tropospheric ozone decreases resulted from coupling between infrared opacity changes and tropospheric photochemistry. This coupling arises due to increases in tropospheric and stratospheric levels of CO_2 and CFM's. This work discusses fully this relatively strong coupling mechanism. It appeared in JGR (February 1983).

(iii) Conducted study using radiative equilibrium calculations (as a function of latitude and altitude) and quasi-geostrophic planetary wave calculations to evaluate the Hines mechanism as a means of relating solar cycle variations with tropospheric climate changes. In 1974, C. O. Hines proposed a mechanism by which the upper atmosphere would be modified by solar flux variations in such a way that the long planetary waves and, hence, tropospheric weather and climate might be modified--a question of interest for decades. In the present work, radiative and planetary wave calculations were used to examine the feasibility of the Hines mechanism. We conclude that the mechanism will not lead to substantive changes in the troposphere but may have significant effects in the upper stratosphere. The work sheds significant new light on the effect of solar UV flux variations on the thermal and dynamic structure of the stratosphere. The work has been submitted to JGR.

(iv) Examination of LIMS data suggests that the odd nitrogen (ON) mixing ratio declines sharply above an altitude of 35 km. The mixing ratio drops from a maximum value of 15-17 ppbv near the peak to values as low as 6 ppbv near the stratopause. This is contrary to what is calculated by most 1-D and 2-D models. Use of the LIMS data in conjunction with the Langley 1-D model has led to the conclusion that the mesosphere is a net global sink for stratospheric ON. (At high latitudes in the polar wintertime, the mesosphere is a source of ON. This downward flux occurs, however, only over a relatively limited geographic area. Consequently, on a global basis, the mesosphere is a net sink for ON.) As a result of this finding, the ON upper boundary conditions of stratospheric models must be substantially revised. Our understanding of the relative roles of transport and photochemistry in establishing ON levels in the upper stratosphere must also be revised. This work has been presented at the 1982 Fall AGU Meeting and is in preparation for publication in JGR.

(v) Preliminary consistency checks on currently accepted stratospheric photochemistry have been made using the Langley 1-D model in conjunction with the LIMS data. Results to date suggest that presently accepted chemistry, rates, and cross sections lead to an underprediction of O_3 at the vernal equinox and at 30°N and altitudes where photochemical equilibrium should prevail. Calculated O_3 values are 30 - 50 percent less than values observed by both the SBUV and LIMS instruments. This suggests that either the chemistry is incomplete or that some of the recommended rates are in substantial error. The photochemical rates can be adjusted within the error bars such that reasonable agreement is obtained. Key rates are identified.

(vi) Work has been conducted to assess the effect of CFM build-up on the stratospheric zonal wind state. Results indicate that zonal winds could be appreciably altered due to perturbed Equator-to-pole thermal gradients which result from the ozone destruction. Zonal winds were found to change by as much as 28 percent. Near the tropical stratopause in the summertime, the additional westerly component, due to the effect of the CFM's, was strong enough to cause a reversal in the summertime easterlies. Such significant changes in the zonal winds suggest the possibility of changes in the climatology of planetary waves in the stratosphere. Such changes should be examined in more detail.

E. Journal Publications:

Callis, L. B.; Natarajan, M.; and Boughner, R. E.: On the Relationship Between the Greenhouse Effect, Atmospheric Photochemistry, and Species Distribution. J. Geophys. Res., Vol. 88, No. C2, Feb. 20, 1983, pp. 1401-1426.

Callis, L. B.; Russell, J. M. III; Natarajan, M.; and Haggard, K. V.: Examination of Wintertime Latitudinal Gradients in Stratospheric NO_2 Using Theory and LIMS Observations. Geophys. Res. Lett., In Press, 1983.

Callis, L. B.; Alpert, J. C.; and Geller, M. A.: An Assessment of Thermal, Wind, and Planetary Wave Changes in the Middle and Lower Atmosphere Due to 11-Year UV Flux Variations. Submitted to J. Geophys. Res., Aug. 1983.

Russell, J. M.; Gordley, L. L.; Remsberg, E. E.; Solomon, S.; and Callis, L. B.: The Variability of Stratospheric and Mesospheric NO_2 in the Polar Winter Night Observed by LIMS. Submitted to J. Geophys. Res., Aug. 1983.

STUDIES OF ODD NITROGEN IN THE EARTH'S ATMOSPHERE

(NAWG-292)

Dr. David W. Rusch, P.I.
Laboratory for Atmospheric and Space Physics
University of Colorado
Boulder, Colorado 80309

ABSTRACT

This research is aimed at improving our understanding of the distribution of nitric oxide and other "odd nitrogen" species in the mesosphere and lower thermosphere. Topics receiving attention include:

1. the extent to which the abundance of mesospheric nitric oxide responds to solar activity, to compositional changes in the lower thermosphere and to electron and proton precipitation;
2. the effects of odd nitrogen produced in particle events on mesospheric and upper stratospheric ozone and;
3. the efficiency of the atmosphere to produce nitric oxide during particle events.

SUMMARY

Work has continued in two main areas. A numerical study with a two dimensional model with coupled photochemistry and dynamics has shown a significant solar cycle variation in NOx in the mesosphere and thermosphere. Considerable amounts of NOx are transported to the stratosphere by the global mean meridional circulation and this excess NOx can lead to significant decreases in ozone concentrations at high latitudes.

In a separate study, the production of nitric oxide in the polar regions

by auroral deposition was found to contribute significantly to the global odd nitrogen budget in the lower thermosphere and upper mesosphere. The objective of these studies is to determine the flux of odd nitrogen into the mesosphere and upper stratosphere and to determine its significance in the global NOx budget.

PUBLICATIONS

The global distribution of thermospheric odd nitrogen for solstice conditions during solar cycle minimum (with J.C. Gerard, R.G. Roble, and A.I. Stewart), J. Geophys. Res., In Press, 1983.

A numerical study of the response of the middle atmosphere to changing solar activity, (with R.R. Garcia, S. Solomon, and R.G. Roble), published in Proceedings of the Second International Symposium on Solar Terrestrial Influences on Weather and Climate, held at Boulder, Colorado, 2-6 August, 1982.

A numerical study of the response of the middle atmosphere to the 11- year solar cycle, (with R.R. Garcia, S. Solomon, and R.G. Roble), Planet. Space Sci., In Press, 1983.

TITLE: Chemistry of Stratospheric and Tropospheric Gases

INVESTIGATORS: Michael B. McElroy, Steven C. Wofsy, Michael J. Prather and Jennifer A. Logan

INSTITUTION: Harvard University, Cambridge, Massachusetts 02138

RESEARCH OBJECTIVES

Our program of theoretical research is designed to investigate factors influencing the chemical composition of the atmosphere, both stratosphere and troposphere. We are continuing to analyze satellite data examining variations in O_3 at 40 km over the past decade, with a companion investigation of data for O_3 in the troposphere. We plan to extend earlier work on chemical and biogeochemical cycles for important trace gases, including CO, CH_4, CO_2 and N_2O emphasizing possible effects on climate and air quality. We are developing a 3-dimensional chemical model, incorporating transport and physical properties obtained from a general circulation model at the Goddard Institute for Space Studies. This collaborative research is intended to provide a framework for defining the chemical composition of the global troposphere.

GCM PROGRESS

The development of a three-dimensional tracer transport model based on the GISS general circulation model has proceeded on several fronts. The original GISS tracer model has been revised to speed computation, to conserve tracer amount, and to include chemistry and diagnostics of chemical processes. We have begun initial tests of atmospheric transport by employing the chlorofluorocarbons, freon-11 and freon-12, as tests of atmospheric circulation (see Lovelock, Nature 230, 379, 1971). The freon series of calculations is now complete and the paper is being drafted. The modelled concentrations accurately reproduce the individual station data from the Atmospheric Lifetime Experiment, including some of the seasonal cycles.

This project required significant interaction between the research groups at Harvard and GISS as we examined the mechanisms responsible for interhemispheric exchange and intrahemispheric redistribution. This series of freon tracer calculations involved several sets of GCM calculations, including different spatial resolutions and physical parameterizations.

The freon experiments allowed only for simplified stratospheric losses. The fully-coupled chemistry of the troposphere is soon to be added to the tracer model. We are presently testing parameterizations for rapid computation of OH concentrations and ozone production as a function of NO_x, CO, O_3, H_2O, temperature, cloud cover, ozone column and latitude. Formal testing of these schemes shows that our method of parameterization will calculate the global distribution of OH concentrations with an rms error of order 8% and a mean error of less than 2%. We expect to begin preliminary tracer calculations with this coupled chemical model sometime this fall.

A detailed study of chemical instabilities in the lower stratosphere was recently completed (Fox, Wofsy, McElroy and Prather, 1982), continuing the initial work of Prather, McElroy, Wofsy and Logan (1979). The set of chemical kinetic equations applicable to the winter stratosphere were found to have more than one solution for the 1981 revision of kinetic data. These multiple solutions were found to occur in the full diurnal model. Solutions with higher concentrations of ClO tend to predominate when the different steady-state solutions are placed in contact with each other. These conditions of multiple equilibria are expected to become more prevalent as the concentration of chlorine in the stratosphere increases with the continued release of anthropogenic halocarbons.

We are examining the idea (McElroy, 1983; Broecker, 1983) that climatically significant fluctuations of CO_2, on time scale of 10^3-10^4 yr, are controlled by variations in oceanic N, and that the concentration of fixed N in the ocean is not in steady state. We are developing a multi-box ocean-atmosphere model to investigate quantitatively the coupling between N, P and atmospheric CO_2.

Analysis of long-term trends for tropospheric ozone is almost complete. While there is evidence that tropospheric ozone may be increasing, there are serious inconsistencies within the data set.

The chemical cycle of NO_x in the troposphere has been examined from both global and regional perspectives. Our estimates for global source strengths are consistent with the rate of removal of NO_x derived from recent atmospheric and precipitation chemistry data. Examination of regional deposition and emissions for oxides of nitrogen demonstrate export of NO_x from industrialized areas of the U.S. to remote parts of North America.

PUBLICATIONS

J.L. Fox, S.C. Wofsy, M.B. McElroy, M.J. Prather (1982). A stratospheric chemical instability. J. Geophys. Res. 87, 11126.

S.C. Wofsy and J.A. Logan (1982) Recent developments in stratospheric chemistry. In Causes and Effects of Stratospheric Ozone Reduction: An Update, National Academy Press, pp. 167-205.

M.B. McElroy (1982) Marine biology: controls on atmospheric CO_2 and climate. Nature 302, 328.

J.A. Logan (1983) Nitrogen oxides in the troposphere: global and regional budgets. J. Geophys. Res., accepted for publication.

J.A. Logan (1983) Comment on 'On the atmospheric input of sulfur into the ocean' by E. Mesaroz. Tellus, accepted for publication.

Biennial Summary Report

NASA Grant NSG-7485

A. "Stratospheric Aeronomy"

B. Donald M. Hunten
The University of Arizona
in collaboration with Lon L. Hood

C. The objectives are to apply one-dimensional modeling of the stratosphere, mesosphere, and troposphere to further an understanding of transport processes, and other interactions. Experience with other planetary atmospheres is brought to bear as well.

D. The 1982 Academy report on the ozone problem called out three areas of concern, in which predictions did not match observations. One of these is a very rapid observed falloff of Fluorocarbon-11 between 20 and 30 km, calling into question our understanding of photochemistry and transport of all materials in this region. Three effects have been identified in all by the community: deeper penetration of solar ultraviolet, slower transport, and our contribution, a second-order effect due to wave and other nonmixing motions, distinct from the commonly-assumed eddy transport (see the Reference). It appears that the discrepancy can be resolved by combining the first and third effects, and the eddy transport parameters do not have to be modified.

Dr. Hood, whose main support is from Grant NSG-7020, has been studying satellite ozone data records, applying techiques from his past work on lunar magnetic data. The work is so far limited to Nimbus 4 data of 1970-72. A known effect of temperature on ozone mixing ratio is confirmed, and there is a strong indication of effects of stratospheric warmings and solar flux changes.

E. D.M. Hunten, A second-order effect of stratospheric vertical motions. Geophys. Res. Lett. 10, 333-5 (1983).

SUMMARY

of

MESOSPHERIC-STRATOSPHERIC WAVES

Asynchronous Tides in the Upper Atmosphere

Principal Investigator: Richard W. Zurek
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

OBJECTIVES: Atmospheric tides are planetary-scale, daily oscillations of the temperature, pressure, and wind fields. The largest of these tides are generated by the direct solar heating of atmospheric trace gases such as ozone and water vapor and by thermal convection from Earth's heated surface. The purpose of this task is to determine the structure and amplitude of one particular class of these atmospheric tides: namely, those asynchronous components which do not follow the sun's apparent westward motion and which are generated by topographic modulation of the surface heating and by the longitudinal variations in the distributions of ozone and water vapor. The vertically propagating asynchronous atmospheric tides grow in amplitude with height, as do their solar-fixed counterparts, and may contribute to the natural variability of upper atmospheric winds and temperature. The objectives of this task are to determine the contribution of the asynchronous tides to this short-period natural variability, to estimate their potential for biasing longer-term averages (over weeks and months) of meteorological fields observed from orbiting spacecraft, and to evaluate their nonlinear dynamical influence on the zonally symmetric circulation of the upper atmosphere.

STATUS: Work began late in FY 83. Those components of the asynchronous atmospheric tides which can propagate vertically and thus grow in amplitude with height have been identified. Work is now focusing on computing the thermal forcing functions for these components using satellite-determined ozone distributions.

Summary Report

Kaichi Maeda

A. Title of Research Task

INVESTIGATION OF THE UPPER ATMOSPHERE DYNAMICS WITH NIMBUS SATELLITE DATA

B. Investigators and Institutions

Principal Investigator: Dr. Kaichi Maeda
Code 961
NASA/Goddard Space Flight Center
Greenbelt, MD 20771

Co-Investigator: Dr. Donald F. Heath
Code 963
NASA/Goddard Space Flight Center
Greenbelt, MD 20771

C. Abstract of Research Objectives

Investigate: (1) the dynamical response of the upper stratosphere to the variations of insolation and solar particles, by analyzing the stratospheric ozone data obtained from the Nimbus-4 BUV measurements, and (2) the global structure of the semi-annual oscillation in the stratospheric ozone based on the analysis of the Nimbus-7 SBUV data.

D. Summary of Progress and Results

(1) Based on the Nimbus-4 BUV data, the north-south hemispheric asymmetries in the stratospheric ozone depletion during two solar flare events (25 January 1971 and 4-9 August 1972) have been presented with theoretical interpretations in NASA X-961-82-2. This paper was accepted for publication in Journal of the Atmospheric Sciences with the condition that the color contour figures are replaced by the line-contour map. The paper is therefore submitted for publication switching from J.A.S. to the Journal of Geophysical Research (blue issue) which accept the color prints under the following title and authors: North-South Asymmetries of Solar Particle Events in the Upper Stratospheric Ozone, K. Maeda, D. F. Heath and T. Aruga.

(2) Hemispheric asymmetry in the upper stratospheric ozone due to the eccentricity of the earth's orbit and tilted spin axis from the ecliptic plane has been confirmed from the Nimbus-7 SBUV data. Further analysis has indicated that the winter hemispheric asymmetry is affected by the orographic difference of the earth's surface between two hemispheres. The results with theoretical interpretations are published in the Journal of the Atmospheric Sciences (see E.)

(3) By means of the spherical harmonic analysis, the global structure of semi-annual oscillation in the stratospheric ozone was presented at the AGU-meeting in June at Baltimore, Maryland. The ozone data are obtained from the Nimbus-7 SBUV measurements but only two years of period, from November 1978 to October 1980. This paper will be submitted to Geophysical Research Letters with the following title and authors: Semi-annual Oscillation of Stratospheric Ozone, K. Maeda, S. K. Kirshner and T. Aruga.

E. Journal Publications

Asymmetries of the Upper Stratospheric Ozone Distribution Between Two Hemispheres, Kaichi Maeda and Donald F. Heath, J. Atmos. Sci., 40, No. 5, 1353-1359, 1983.

B. THREE DIMENSIONAL MODELS

Three-dimensional Dynamical and chemical modelling of the Upper Atmosphere

P.I.: Professor R.G. Prinn, M.I.T., Cambridge, MA
Co-I.: Dr. F. Alyea, Dr. D. Cunnold, Georgia Tech., Atlanta, GA

OBJECTIVES: Complete the development of a spectral 3-dimensional quasi-geostrophic model of the global atmosphere which incorporates on-line some 40 chemical reactions governing stratospheric ozone concentrations (the model possesses 32 levels between the surface and mesopause (.0035 mb) and has zonal wavenumbers 0-18). Utilize this model and a lower resolution (wave-numbers 0-6) predecessor in studies of the coupled radiative-chemical-dynamical behavior of the upper atmosphere.

SUMMARY OF 1982-1983 PROGRESS: A number of runs of the new model were made over the October 1982 - June 1983 time frame. The model now successfully simulates the observed zonal-mean climatology of the stratosphere and meso-sphere including closure of the polar night and summer jets and reversal of the pole-to-pole temperature gradient above the stratopause To achieve the realistic mesospheric zonal-mean climatology it was necessary however to include prescribed horizontal diffusion terms of the form $A\nabla^2\xi$ and $A\nabla^2 T$ in the potential vorticity and thermodynamic equations respectively (typically $A \approx 6 \times 10^6 (\ell n\ P(b)/\ell n\ P_{top}(b))^6\ m^2 sec^{-1}$). The new model is presently being transferred to the NASA-GSFC Cyber 205 computer--progress in this latter task has been slower than expected.

Three masters theses and one doctoral thesis have been completed in 1982-1983 as a part of this project. Olaguer (S.M. thesis, MIT) has computed the residual-mean circulation of the stratosphere using the output from a recent run of our 0-6 wave model. Weisenstein (S.M. thesis, MIT) has constructed a two-dimensional global chemical model in which transport is dominated by advection by the residual-mean circulation and successfully applied this model to prediction of the global spatial and temporal distributions of selected halocarbons. Trepte (S.M. thesis, Georgia Tech.) has examined the maintenance of the planetary wave structure of ozone using SBUV ozone data and TIROS-N temperature and geopotential height data for December, 1978 - May 1979. Finally, Golombek (Ph.D. thesis, MIT) has developed a remarkably efficient 3-D global model with prescribed circulation for use in chemical studies of the troposphere and lower stratosphere. The model was successfully applied to prediction of the spatial and temporal distributions of four halocarbons and nitrous oxide.

Summary Report

A. Title: Stratospheric Dynamics

B. Investigators and Institutions: R. E. Young, Principal Investigator; NASA-Ames Research Center, Moffett Field, CA 94035

C. Abstract of Research Objectives:

Stratospheric dynamical and radiative processes are simulated with a 3-dimensional primitive equation model. The principal goal is to study the dynamical and radiative processes which are important in transporting momentum, energy, and trace species between different regions of the atmosphere. Current research focuses on the role synoptic scale baroclinic waves play in forcing planetary scale waves which penetrate into the stratosphere, and the importance of wave-wave coupling on the dynamics of the stratosphere.

D. Progress and Results:

During 1982, results from the 3-dimensional stratosphere model were compared to previously published computations in order to validate the model. This validation procedure uncovered a numerical problem which caused spurious amplitude buildup in the tropics for highly nonlinear situations, and eventual computational instability. Most of 1982 and part of 1983 were spent in identifying and correcting the cause of the computational difficulties.

Subsequent work has concentrated on application of the model to the question of forcing by synoptic scale baroclinic waves of planetary scale waves through wave-wave coupling. Although baroclinic processes are most important in the troposphere, forced planetary scale waves can propagate vertically and penetrate well into the stratosphere. Model runs have shown that under certain circumstances, wave-wave coupling forces growth rates of the planetary scale baroclinic modes which are comparable to the growth rates of the most unstable baroclinic modes. Such results are consistent with the computational results obtained by Gall et al. (J. Atm. Sci., 36, 1979). The computed structures of the planetary waves are qualitatively consistent with several of the features seen in observed eastward travelling planetary waves of the southern winter hemisphere (Mechoso and Hartmann, J. Atm. Sci., 39, 1982).

Initial model results were reported at the Fourth Conference on Atmospheric and Oceanic Waves and Stability, March 22-25, 1983, Boston, Mass.

Report to NASA Upper Atmosphere Research Program

Research Summary for 1982-1983

TITLE: Wave Dynamics and Transport in the Stratosphere

INVESTIGATORS: Principal Investigator: Prof. J. R. Holton
University of Washington

Co-Investigator: Prof. C. B. Leovy
University of Washington

ABSTRACT

This grant supports a program of theoretical studies and numerical modeling designed to elucidate the dynamics of large scale motions in the stratosphere and their role in the transport of heat, momentum, and trace chemical substances. The emphasis of the project is on the physics of wave motions and the role of wave mean-flow interactions in maintaining the observed heat, momentum and trace species budgets.

SUMMARY OF PROGRESS

We have continued to develop and improve our 3-d numerical model of the global middle atmosphere. this model is a truncated semi-spectral primitive equation model which includes the zonal mean flow plus two zonal planetary wave components. During 1982-83 we have concentrated on investigating the roles of wave drag and diffusion due to breaking internal gravity waves.

It has recently become clear that there is strong mechanical dissipation in the middle atmosphere due to the breaking of vertically propagating internal gravity waves. We have developed a simple parameterization scheme, based on an idea of Lindzen (1981), to incorporate the effects of gravity wave drag and diffusion into our global model. For a simple specified spectrum of wave phase speeds the model produces reasonably realistic mean wind and temperature distributions for both summer and winter solstices. In addition, sudden stratospheric warmings produced in the model are accompanied by mesospheric coolings which can be explained in terms of the relaxation of the polar mesosphere towards a radiative equilibrium temperature distribution due to the reduction of gravity wave transmission which occurs in the stratosphere during the sudden warming.

Studies of ozone transport utilizing the global 3-d model have shown that transport into the lower polar stratosphere is greatly enhanced during a sudden warming event. We are developing diagnostic techniques which we believe will provide a clear measure of the net wave-transport effects.

JOURNAL PUBLICATIONS (1982-1983)

Holton, J. R., 1982: The role of gravity wave induced drag and diffusion in the momentum budget of the mesosphere. J. Atmos. Sci., 39, 791-799.

Holton, J. R., 1983: The influence of gravity wave breaking on the general circulation of the middle atmosphere. J. Atmos. Sci., 40, (in press).

Palmer, T. N., 1982: Properties of the Eliassen-Palm flux for planetary scale motions. J. Atmos. Sci., 39, 992-997.

Palmer, T. N. and C.-P. Hsu, 1983: Stratospheric sudden coolings and the role of nonlinear wave interactions in preconditioning the circumpolar folw. J. Atmos. Sci., 40, 909-928.

A. Title: General Circulation with Chemistry Modeling (SGCCM)

B. Investigators and Institutions:

Dr. M. A. Geller (Principal Investigator)
NASA/GSFC

Dr. E. Kalnay
NASA/GSFC

Dr. M. R. Schoeberl
NASA/GSFC

Dr. D. F. Strobel
NRL

Dr. J. Shukla
NASA/GSFC

Dr. R. S. Stolarski
NASA/GSFC

C. Abstract of Research Objectives:

The goal of this project is to increase our understanding of the fully interactive general circulation of the stratosphere including the mechanics of constituent transport and the dynamical and radiative coupling of the troposphere and stratosphere. This program of research includes general circulation modeling of the dynamical, chemical, and radiative structure of the upper atmosphere; analysis of upper atmosphere general circulation and constituent concentration data; and mechanistic studies of upper atmospheric processes for the purpose of developing sufficient understanding to include them properly in general circulation models of the upper atmosphere.

D. Summary of Progress and Results 1982-83

Gridpoint Model

Our principal achievement during this period was making quite successful week long forecasts of the major stratospheric warming in February 1979 and the minor stratospheric warming in January 1979 using a 19-level (surface-60 km) 4° (latitude) x 5° (longitude) global circulation model. These forecasts used observed initial conditions from satellite data. We also have been running a 45-level (surface-90 km) 9° (latitude) x 10° (longitude) global circulation model for climatology modeling.

Spectral Model

Our spectral model is producing good looking symmetric temperature and wind states. We have also produced reasonable looking planetary wave distributions.

General Circulation with Chemistry Modeling (SGCCM)

Analysis of Observations

We have analyzed NOAA/NMC satellite data for the four Northern Hemisphere winters 1978-79, 1979-80, 1980-81, and 1981-82. We have published papers on the four year averaged winter monthly statistics and are submitting a paper on the interannual variability. We have also analyzed the complete four years of data for monthly means and time series. We have also computed correlations between Eliassen-Palm flux divergence and the time rate of change of the mean zonal flow for these four Northern Hemisphere winters.

Mechanistic Studies

(1) A paper has been written and accepted on the relative roles of planetary wave forcing by orography and by diabatic heating.

(2) A paper showing importance of non-zonal forcing and propagation of gravity waves in the winter mesosphere has been written and is in press.

(3) A simple model of ozone advection by the observed wavenumber five has been constructed and gives results in excellent agreement with TOMS observations.

(4) A conservative form of Matsuno's potential vorticity equations has been derived.

(5) Models of inert tracer transport and ozone transport have been constructed and run to enhance our understanding of three-dimensional transport, in general, and ozone transport, in particular.

E. Journal Publications:

(1) Chao, W. C., and M. A. Geller, "Utilization of normal mode initial conditions for detecting errors in the dynamics part of primitive equation global models," Mon. Wea. Rev., 110, 304-306, 1982.

(2) Geller, M. A., "Dynamics of the middle atmosphere (tutorial lecture)," Space Sci. Rev., 34, 359-375, 1983.

(3) Geller, M. A., M. -F. Wu, and M. E. Gelman, "Troposphere-stratosphere (surface - 55km) monthly winter general circulation statistics for the Northern Hemisphere - four year averages," J. Atmos. Sci., 40, 1334-1352, 1983.

(4) Alpert, J. C., M. A. Geller, and S. K. Avery, "The response of stationary planetary waves to tropospheric forcing," J. Atmos. Sci., (in press), 1983.

(5) Schoeberl, M. R. and D. F. Strobel, "Nonzonal gravity wave breaking in the winter mesosphere," Proceedings of the U.S.-Japan Seminar on Dynamics of the Middle Aymosphere, (in press), 1983.

(6) Geller, M. A., "Modeling the middle atmosphere circulation," Proceedings of the U.S.-Japan Seminar on Dynamics of the Middle Atmosphere, (in press), 1983.

(7) Schoeberl, M. R., and A. J. Krueger, "Medium scale disturbances in total ozone during Southern Hemisphere summer," Bull. Amer. Meteor. Soc., (in press), 1983.

(8) Schoeberl, M. R., "A note on the conservation properties of Matsuno's potential vorticity equations," (submitted to J. Atmos. Sci.), 1983.

(9) Chao, W. C., and M. R. Schoeberl, "A note on the linear approximation of gravity wave saturation in the mesosphere," (submitted to J. Atmos. Sci.), 1983.

(10) Geller, M. A., M.-F. Wu, and M. E. Gelman, "Troposphere-stratosphere (surface-55 km) monthly winter general circulation statistics for the Northern Hemisphere-interannual variations," (submitted to J. Atmos. Sci.), 1983.

(11) Schoeberl, M. R., and R. S. Lindzen, "Numerical simulation of the point jet barotropic instability including wave-mean flow interaction," (to J. Atmos. Sci.), 1983.

(12) Callis, L. B., J. C. Alpert and M. A. Geller, "An assessment of thermal, wind, and planetary wave changes in the middle and lower atmosphere due to the 11-year UV flux variations," (submitted to J. Geophys. Res.), 1983.

SENSITIVITY OF THE STRATOSPHERIC CIRCULATION TO PARAMETERIZED TROPOSPHERIC PROCESSES

Principal Investigator: David A. Randall
Code 911
Global Modeling and Simulation Branch
NASA/Goddard Space Flight Center
Greenbelt, MD 20771

Co-Investigators: David M. Straus
Code 911
Global Modeling and Simulation Branch
NASA/Goddard Space Flight Center
Greenbelt, MD 20771

J. Shukla
Code 911
Global Modeling and Simulation Branch
NASA/Goddard Space Flight Center
Greenbelt, MD 20771

Marvin Geller
Code 964
Atmospheric Chemistry Branch
NASA/Goddard Space Flight Center
Greenbelt, MD 20771

Abstract of Research Objectives: The objectives of this research are to extend the upper boundary of the GLAS Climate Model to the 1 mb level, and to investigate the sensitivity of the simulated stratospheric circulation to parameterized boundary layer and cloud processes, by comparing results from the GLAS and UCLA GCMs.

Summary of Progress and Results: The 15-level, stratospheric version of the UCLA GCM has been made to run on the GSFC Cyber 205, and extensive efforts have been expended to improve the model's running speed through vectorization. A simple vertical diffusion parameterization, based on the work of Mahlman, has been added to provide necessary damping in the upper stratosphere. The potential-enstrophy-conserving version of the GLAS Climate Model, running on the GSFC Amdahl 470 V/6, has been endowed with a stratosphere, by increasing the number of levels from 9 to 15, raising the model top to 1 mb, and adopting a pressure coordinate system above 100 mb. Ozone has been added as an optional prognostic variable, using a fourth-order horizontal advection scheme, and the simple Schlesinger-Mintz photohemistry parameterization. In order to allow arbitrary ozone distributions, the radiation parameterization of the model has been replaced by the Schlesinger-Katayama parameterization. We also are experimenting with an improved version of the GLAS solar radiation parameterization (developed by Prof. R. Davies of Purdue University), and with a new terrestrial radiation parameterization (developed by Dr. Harshvardhan of Code 915). The latter shows real promise in at least partially correcting the "cold pole" problem. Great care has been taken to ensure that the GLAS and UCLA models have the same finite-difference schemes, and differ only in their physical parameterizations for clouds and the planetary boundary layer. Postprocessing and plotting packages have been created for both models. Currently, the models are being compared in short test runs, in preparation for extended production runs.

In the near future, final choices will be made for the parameterizations of radiation and vertical diffusion, based on the short runs currently in progress. A number of initial conditions will be created from the FGGE data. Production runs will be made to produce January and July simulations. The results will be analyzed to study the differences between the two models, as reflected in vertically propagating waves (tropics and mid-latitudes), upwelling terrestrial radiation at the tropopause, moisture transport by the Hadley circulation, and the atmospheric semidiurnal tide.

Journal Publications: None.

SUMMARY OF RESEARCH TASK

A. Title: Three-Dimensional Model Studies of Stratospheric Transport Processes and Comparisons with Large, Global Sets of Satellite Data

B. Investigators and Institution:

Dr. William L. Grose	Principal Investigator
W. Thomas Blackshear	Co-Investigator
John E. Nealy	Co-Investigator
Dr. Ellis E. Remsberg	Co-Investigator
Dr. James M. Russell III	Co-Investigator
Richard E. Turner	Co-Investigator
Denise S. Graves	Co-Investigator
	NASA Langley Research Center
	Hampton, VA 23665

C. Abstract of Research Objectives: A 3-D primitive equation general circulation model will be used to generate wind and temperature data over seasonal and/or annual cycles. These data will then be used as input to a separate 3-D transport model, including realistic chemistry to simultaneously evolve the distributions of the important stratospheric trace constituents. The model simulations will be analyzed to determine the relative importance of various transport processes. Comparisons of model simulated species distributions, meteorological parameters, and dynamical quantities will be made with corresponding results derived from global data sets from experiments on the Nimbus 7 satellite. Particular emphasis will be devoted to Northern Hemisphere winter conditions. These studies will provide a consistent set of model simulated data for important stratospheric trace species over seasonal and/or annual cycles. Comparison of model results with global data sets will aid in assessing the validity of current theoretical models and identify areas requiring improvement in model formulation. Model results also assist in analysis and interpretation of the measured data sets. Model simulations can also be used to evaluate and optimize sampling strategies for future missions.

D. Summary of Progress and Results:

1. Completed the first 3-D global model simulation of simultaneous multi-species transport during the Northern Hemisphere winter. Simulated distributions of O_3, HNO_3, and NO_2 have been compared with LIMS data. Total column ozone distributions have been compared with BUV data. Extremely favorable comparisons demonstrate the validity of transporting chemical "families" rather than individual species.

2. Analyses of transport processes during winter simulation have been conducted. Comparisons with results from other 3-D models show good agreement.

3. Completed long-term simulation of ozone transport using a linearized chemistry. Results provide insight into relative roles of transport and chemistry in various regions of the stratosphere. Evolving role of transport during seasonal transitions in the stratosphere has been examined.

4. Completed study of the role of subtropical thermal forcing in initiating large-scale disturbances which propagate into the stratosphere. Demonstrated that subtropical thermal anomalies produce mid-latitude quasi-stationary disturbances. Also demonstrated that baroclinic instability development in mid-latitudes can be induced as a result of subtropical thermal forcing.

5. Analyzed primitive equation model simulated stratospheric warming. Completed analysis of 1979 stratospheric warming using LIMS temperature data. These temperature data have been used to derive geopotential height, winds, heat and momentum fluxes, Eliassen-Palm flux, and potential vorticity. Comparisons of the actual and simulated warmings have been conducted to understand the relevant processes occurring during a warming event.

6. LIMS temperature data have been utilized in conjunction with NMC and Berlin meteorological data to derive dynamical quantities. These derived quantities have been compared for selected days with equivalent results from SAMS, SSU, and conventional meteorological analysis. Results provide an assessment of the quality of both the data and the derived products.

E. Journal Publications:

Grose, W. L.; Blackshear, W. T.; and Turner, R. E.: The Response of a Non-Linear Time-Dependent, Baroclinic Model of the Atmosphere to Tropical Thermal Forcing. Submitted to Quart. J. Roy. Meteorol. Soc.

Kurzeja, R. J.; Haggard, K. V.; and Grose, W. L.: Numerical Experiments With a General Circulation Model Concerning the Distribution of Ozone in the Stratosphere. Submitted to J. Atmos. Sci.

Grose, W. L.; Nealy, J. E.; Turner, R. E.; and Blackshear, W. T.: Transport of Trace Species in the Stratosphere - Results of a Northern Hemisphere Winter Simulation. Presented at Fourth Conference on the Meteorology of the Upper Atmosphere, Boston, MA, Mar. 22-25, 1983. Manuscript in preparation for submittal to J. Atmos. Sci.

Nealy, J. E.: Monte-Carlo Calculation of Stratospheric Trace Species from Candidate Satellite Measurement Sets. Manuscript in preparation for J. Atmos. Chem.

Planetary Wave Models of
Stratospheric and Mesospheric Dynamics

Dr. Darrell F. Strobel, Principal Investigator
Dr. Mark R. Schoeberl, Co-Investigator (on leave)

Naval Research Laboratory, Washington, D.C. 20375

The Atmospheric Dynamics Section in the Geophysical and Plasma Dynamics Branch at the Naval Research Laboratory is currently engaged in theoretical investigations of stratospheric and mesospheric dynamics. The work proposed by Drs. Darrell F. Strobel (Principal Investigator) and Mark R. Schoeberl (Co-Investigator) includes: (1) study of the quasi-steady circulation of the stratosphere and mesosphere, (2) study the effects and mechanisms of sudden stratospheric warmings, (3) evaluate the response of the mean circulation to stratospheric ozone reductions, (4) study minor constituent transport by the mean circulation and planetary waves in the middle atmosphere, and (5) develop simplified chemical models.

Ozone transport was calculated for steady, dissipative planetary waves using the Eulerian, Lagrangian mean, and residual circulation. A lagrangian model of parcel dynamics was used to interpret planetary wave-photochemistry interation. In chemically active regions the mean field ozone changes were found to be significant only where there are large gradients in chemical sources and sinks along parcel trajectories. The largest changes in the mean field were found in the lower stratosphere and are due to the Lagrangian mean advection. When the Lagrangian mean advection is approximated by the residual circulation, errors in the transport velocities as large as 30% may occur.

The stresses generated by breaking gravity waves in the mesosphere were calculated with a numerical model of steady vertically propagating gravity waves that includes wavelength dependent radiative dissipation and turbulent viscosity and conduction. The principal findings were (1) waves do not break for $|\bar{u}-c|$ values < 20 m s^{-1} as radiative damping prevents wave amplitude growth with altitude for short vertical wavelengths; (2) the downward heat flux due to turbulence of breaking waves and turbulent heating through loss of wave energy could severely affect the global radiative energy balance; and (3) predicted zonal deceleration for steady breaking waves is stronger than required by Apruzese et al. (1982) for the mean circulation. Gravity wave breaking may be an intermittent process; otherwise, gravity wave stresses would produce an adiabatic mesosphere with a zonal mean velocity close to the phase speed of the breaking wave. Diffusive transport of constituents and potential temperature by breaking gravity wave turbulence was shown to be important. In cases of nitric oxide and atomic oxygen the vertical eddy diffusion coefficients were shown to be sensitive functions of their respect chemical loss rates in the mesosphere and lower thermosphere.

The balance of potential enstrophy and its relationship to vacillation cycles and the sudden warming was studied for a β-channel model of the stratosphere. It was shown that the mean flow cannot be steady in the presence of large-amplitude quasi-geostrophic waves [~ 1-1.25 geopotential kilometers (gpkm)] when any dissipation is present, and the maximum wave amplitude allowed is ~2 gpkm. If wave forcing (transience plus dissipation) is artifically maintained the mean flow decelerates slowly at first then explosively as the potential vorticity gradient of the basic state is wiped out over the channel. This process is called wave saturation. The initial phase of the explosive deceleration resembles both the observed and modeled mean flow evolution during a sudden stratospheric warming.

During 1982 and 1983 the following manuscripts were published and submitted:

Lindzen, R.S., and M.R. Schoeberl, A note on the limits of Rossby wave amplitudes, J. Atmos. Sci., 39, 1171-1174, 1982.

Schoeberl, M.R., Vacillation, sudden warmings, and potential enstrophy balance in the stratosphere, J. Atmos. Sci., 39, 1862-1872, 1982.

Apruzese, J.P., M.R. Schoeberl, and D.F. Strobel, Parameterization of IR cooling in a middle atmosphere dynamics model. 1. Effects on the zonally averaged circulation, J. Geophys. Res., 87, 8951-8966, 1982.

Schoeberl, M.R., Wave-mean flow statistics, J. Atmos. Sci., 39, 2363-2368, 1982.

Schoeberl, M.R., A study of stratospheric vacillations and sudden warmings on a β-plane. Part 1: Single wave-mean flow interaction, J. Atmos. Sci., 40, 769-787, 1983.

Rood, R.B., and M.R. Schoeberl, A mechanistic model of Eulerian, Lagrangian-mean, and Lagrangian ozone transport by steady planetary waves, J. Geophys. Res., 88, 5208-5218, 1983.

Schoeberl, M.R., D.F. Strobel, and J.P. Apruzese, A numerical model of gravity wave breaking and stress in the mesosphere, J. Geophys. Res., 88, 5249-5259, 1983.

Schoeberl, M.R., and D.F. Strobel, Nonzonal gravity wave breaking in the winter mesosphere, Proc. U.S.-Japan Seminar on Dynamics of the Middle Atmosphere, Terrapub., Japan, in press, 1983.

Kaye, J.A., and D.F. Strobel, Enhancement of heavy ozone in the earth's atmosphere?, J. Geophys. Res., in press, 1983.

Rood, R.B., and M.R. Schoeberl, Ozone transport by diabatic and planetary wave circulations on a β-plane, J. Geophys. Res., in press, 1983.

Apruzese, J.P., D.F. Strobel, and M.R. Schoeberl, Parameterization of IR cooling in a middle atmosphere dynamics model. 2. Non-LTE radiative transfer and the globally averagedf temperature of the mesosphere and lower thermosphere, J. Geophys. Res., submitted, 1983.

Title of Research Task: Understanding the Influence of Initial Conditions, Boundary Conditions, Topography, and Irreversible Processes on the Intensity and Mass Transfer of Tropopause Folding Events

Investigators and Institutions: L.Pfister and E.F. Danielsen, NASA Ames Research Center, Moffett Field, CA; T. Warner, Pennsylvania State University, University Park, PA.

Research Objectives:

Tropopause folds are upper tropospheric fronts associated with midlatitude baroclinic storms. They are believed to be responsible for the bulk of stratosphere-to-troposphere downward mass transfer in midlatitudes, and an unknown amount of upward transfer. The two major objectives of this work are: 1) to understand the effects of topography, initial conditions, moist processes, and mixing processes on the development of tropopause folds, with the ultimate aim of extending downward mass transfer estimates for individual folds over the data-rich North American continent to a global budget; and 2) to gain a better understanding of upward transfer. We will approach this by numerically simulating the phenomenon with the existing Penn State mesoscale model. This will be done in two stages. The first will involve a channel model simulation with simplified initial conditions in order to isolate the effects of topography alone. Such a channel simulation, with its reduced horizontal domain size, will also allow more simulations to be performed with available computer resources. In the second stage, observed examples of tropopause folds will be simulated with realistic initial and boundary conditions, and irreversible processes included.

Progress and Results:

This project is new, so progress is limited. However, we have made progress in two areas. First we have made most of the modifications necessary to run the Penn State mesoscale model as a channel model with cyclic boundary conditions. Second, we have selected the April 18, 1973 case of tropopause folding from the meteorological archives for simulation. One of us (EFD) has also produced subjective analyses on isentropic surfaces for this case, which will be helpful in generating initial conditions, verifying the simulation, and understanding the phenomenon.

Publications: None to this date

C. MOLECULAR CALCULATIONS

A. Title: Computational Investigation of Reactive Molecules

B. Investigators: D. H. Phillips, NASA Langley Research Center
J. A. Jafri, Old Dominion University Research Foundation
J. H. Deitrich, National Research Council Associate

C. Abstract of Research Objectives

This research utilizes a computational approach based on the quantum mechanical Shrodinger equation to obtain information on the photochemical properties and processes of radicals and other short-lived molecular species which are difficult to study by experimental techniques. The research includes both the spectroscopic properties of radicals (like the FO molecule) which may be important to the upper atmosphere as well as weak complexes such as that formed by OH and HO_2 which may affect reaction mechanisms.

D. Summary of Progress and Results

Calculations on the FO molecule have been completed and a paper has been written describing the results. The FO molecule may be produced in the atmosphere from the flourine atoms in anthroprogenically produced fluorocarbons. Although the presence of this radical was inferred from several different kinds of experiments, experiments designed to directly detect the molecule by its ultraviolet and electron paramagnetic spectrum failed repeatedly. Although the molecule was finally detected in the gas phase by Canadian researchers using infrared spectroscopy, the nature of the excited electronic states which would be involved in photochemical processes remained a mystery. The calculations demonstrated that the ultraviolet spectra was diffuse and that every photon absorbed would result in the molecule being broken down into its constituent atoms.

Calculations on the complex between OH and HO_2 were initiated in order to determine if such a complex is responsible for the unusual temperature dependence of this radical-radical reaction. The calculations were initiated using a method which simultaneously determines the energy of the complex and the derivatives of the energy with respect to changes in the geometry of the complex. The current software utilizes a state function which allows mixing of unphysical states into the description however, and an analysis of the results indicated that this spin contamination is reducing the reliability of the results. The calculations have been suspended temporarily while software which utilizes a more general wavefunction is obtained and implemented on the Langley Research Center computers.

A. Title: Computational Chemistry of Methane Oxidation Species

B. Investigators: D. H. Phillips, NASA Langley Research Center
C. F. Jackels, Wake Forest University
J. H. Deitrich, National Research Council Associate
J. A. Jafri, Old Dominion University Research Foundation

C. Abstract or Research Objectives

This research is to determine the photochemical properties of processes of radicals and other short-lived molecular species produced by the oxidation of atmospheric methane (CH_4). The research utilizes a computational approach based on the quantum mechanical Shrodinger equation to obtain chemical information on short-lived molecules which are difficult to investigate by experimental techniques. The emphasis of the research has been on the excited states of the methoxy (CH_3O) and methyl peroxy (CH_3O_2) radicals. These molecules are the first carbon containing molecules produced in the chain of reactions by which methane from natural biogenic sources is ultimately reduced to carbon dioxide (CO_2) and HO_x radicals which participate in the photochemical cycles of ozone, NO_x, SO_2, and other atmospheric trace species. This research is to determine the effects of photolysis of CH_3O_2 on atmospheric chemistry and to develop an understanding of the spectra of CH_3O and the limitations on the use of resonance fluorescence to detect this radical species in the atmosphere.

D. Summary of Progress and Results

1. The Methoxy Radical

Initially, semiquantitative calculations were used to characterize the eight lowest energy (valence) states of CH_3O. This was followed by calculations of quantitative accuracy on the (X^2E) ground state and on the $^2A_1$ state responsible for the observed fluorescence and adsorption in the near ultraviolet region of the spectrum. The results confirmed the interpretation of the most recent spectroscopic experiments on this molecule and provided additional information on the character of the symmetric vibrational states based on each of these electronic states, as well as on the dissociation energy of the molecule. Most recently the crossings between the $^2A_1$ state and a group of three states ($^2A_2$, $^4A_2$, and ^4E) have been determined. These states lead to predissociation of the molecule and limit accurate use of resonance fluorescence to wavelengths longer than about 280 nanometers.

2. The Methyl Peroxy Radical

The observed absorption of the CH_3O_2 molecule peaks in the portion of the ultraviolet wavelengths which are shielded by ozone absorption in the lower atmosphere, but tails off toward the near ultraviolet region which is not shielded. The results of the light absorption depend on the nature of the excited state potential energy curves which are not determined by experiment. Recently completed calculations indicate that the excited states responsible for the light absorption are unstable (repulsive) toward breakup of the molecule into CH_3O + O. Thus any absorption of unshielded solar ultraviolet will convert CH_3O_2 into methoxy plus an oxygen atom which ultimately combine the molecular oxygen to form an ozone molecule. The excited states are metastable with respect to breakup into the methyl (CH_3) radical and O_2 so that this reaction which simply leads to reformation of CH_3O_2 is not very probable and can only occur at solar wavelength present in the stratosphere.

E. Journal Publications

A Theoretical Potential Energy Surface Study of Several States of the Methoxy Radical, by C. F. Jackels, Journal of Chemical Physics 76, pp. 505-515 (1982).

A. TITLE: Molecular Properties and Reaction Rates for Stratospheric Research

B. INVESTIGATOR: R. L. Jaffe
NASA-Ames Research Center

C. OBJECTIVES: Compute reliable chemical rate constants and molecular properties (such as spectra) required for stratospheric models and experiments.

D. RESULTS: Two theoretical studies of the ozone vibrational spectrum have been carried out. In the first study, the harmonic band intensities have been completed. It was found that extensive electron correlation effects had to be included in the wavefunctions in order to determine reliable intensity factors. In the second study accurate potential energy and dipole moment surfaces were computed using large-scale multiconfiguration self-consistent field (MCSCF) wavefunctions similar to those used above. These data have been used by S. Adler-Golden (Spectral Sciences Inc.) to calculate Einstien coefficients for ozone chemiluminescence. He concluded that anharmonic cross terms between normal modes made major contributions to the observed line intensities.

The OH Mienel system which contributes to the visible air glow has been studied as a possible source of the emissions observed by the Space Shuttle and atmosphere explorer satellites. The results of this study may also prove useful to studies of stratospheric research and are therefore presented here. The OH air glow, arises from the reaction $H + O_3 \rightarrow OH + O_2$ which produces highly vibrationally excited OH radicals. The excited OH molecules undergo high overtone transitions (v =3-5) to lower vibrational levels. We have computed a highly accurate dipole moment function for OH and determined the Einstein coefficients for all possible vibration-rotation transitions within the ground electronic state manifold.

E. Publications

C. W. Bauschlicher, Jr. A. Komornicki and B. Roos, "On the N-N Bond in Dinitrogen Tetroxide", J. Am. Chem. Soc. 105 745 (1983).

S. R. Langhoff, R. L. Jaffe, J. H. Yu and A. Dalgarno, "The Surface Glow of the Atmosphere Explorer C and E Satellites". Geophys. Res. Lett. 10, 896 (1983).

B. R. Fredkin, A. Komornicki, S. R. White, and K. R. Wilson "Ab Initio Infrared and Raman Spectra", J. Chem. Phys. to be published (1983).

IV. DATA ANALYSIS

A. INTERPRETATION OF SATELLITE DATA

B. INTERPRETATION OF AIRCRAFT AND BALLOON DATA

C. INTERPRETATION OF SPECTRAL DATA

A. INTERPRETATION OF SATELLITE DATA

Title: Ozone Data Analysis and Empirical Modeling (FY 1982, 1983)

Upper Atmosphere Data Analysis (FY 1984)

Investigators: Principal Investigator: Dr. Carl A. Reber
Co-Investigators: Dr. Sushil Chandra
Dr. John E. Frederick
Mr. Ernest Hilsenrath
Goddard Space Flight Center
Greenbelt, MD 20771

Abstract of Objectives

A basic need of upper atmosphere research is to understand the nature and behavior of the distribution of stratospheric ozone and other related parameters. The ability to assess and evaluate possible man-made modifications of the ozone distribution and density requires the precise knowledge of (1) the natural morphology of ozone, (2) its variations over long and short time scales, and (3) the causes of these variations. The first aspect of the stratospheric analysis effort is the organization of the available data. This is being done in part through the use of an analytical empirical model in which the various parameters are expressed in Fourier series and spherical harmonics representing time, latitude and longitude. A least squares analysis of the data is then used to derive the relevant coefficients and thus isolate systematic geophysical variations. With the systematic variations in hand, nonsystematic long and short term variations in the data are more easily extracted and analyzed for geophysical implications. The existing data will be analyzed for geophysical implications and more data from Nimbus 7 will be incorporated into the analysis as they become available. In particular, latitudinal/seasonal and solar effects will be looked at carefully, incorporating spectral analysis and correlation analysis techniques. Intercomparison of data sets will continue, to discover and reduce systematic uncertainties in these sets.

Summary of Progress and Results

Analysis of Nimbus 4 and Nimbus 7 ozone data in the upper stratosphere revealed a well-defined annual cycle which is in general agreement with photochemical calculations incorporating variations in solar illumination conditions and temperature. At pressures between 5.0 and 0.5 mb the low winter temperatures at mid-latitudes lead to an enchanced mixing ratio over that which prevails in summer. Below 40-45 km the observed winter maximum tends to be greater than one-dimensional model predictions and indicates the action of transport processes. Examination of pressure-latitude cross sections of the ozone mixing ratio reveals an interannual variability which is especially pronounced in the winter season. Such long term natural changes will inhibit attempts to isolate trends of anthropogenic origin in present and future satellite data bases.

Title: Ozone Data Analysis and Empirical Modeling (FY 1982, 1983) and Upper Atmosphere Data Analysis (FY 1984), C. A. Reber, P.I.

Summary of Progress and Results (con't)

Satellite ozone observations on a regional scale were analyzed in conjunction with rocket observations of ozone and analyses of geopotential height field derived by the NMC. An ozone depletion of about 25% in the 5-10 mb height range was observed in the rocket data over Wallops Island (38°N, 75°W) over a 10 day period. A concurrent change was observed in the stratospheric ozone fields derived from Nimbus 7 SBUV data. Examination of the NMC analyses indicated that the stratospheric polar vortex elongated and moved southeastward, bringing air from high latitude to Wallops Island, and displacing air that originated from lower latitudes. A photochemical cause for the ozone changes is ruled out because of the large amounts of a catalytic species that would be required. In addition wind data over the observation site was approximately geostrophic when compared to the height fields. This further suggests the conclusion that the ozone changes observed can be explained by changes in the ozone transport.

Journal Publications

Reber, C. A., and F. T. Huang, Total ozone-solar activity relationship, J. Geophys. Res., 87, 1313-1318, 1982.

Hilsenrath, E., Ozone variations observed during the International Ozone Rocketsonde Intercomparison, Adv. Space Res., 3, No. 7, 1983.

Frederick, J. E., F. T. Huang. A. R. Douglass, and C. A. Reber, The distribution and annual cycle of ozone in the upper stratosphere, J. Geophys. Res., 88, 3819-3828, 1983.

Observed and Theoretical Variations of Atmospheric Ozone

Principal Investigator: Julius London
University of Colorado, Boulder

Abstract of research objectives

The research program discussed here is designed to take advantage of the increased availability of complementary sets of ozone measurements to provide additional physical understanding of the causes of observed space and time (periodic and aperiodic) ozone variations. Since these variations originate primarily in the stratosphere, the studies focus on analysis of Umkehr, ozonesonde and satellite profile measurements in an attempt to determine the association between ozone variations, photochemistry and stratospheric circulations. In particular, a theoretical model is being developed to explain the observed tropical quasi-biennial oscillation in stratospheric ozone.

During the course of our present research, Umkehr, ozonesonde and satellite observations were used to determine the height/latitude distributions of the amplitude and phase of the periodic components of the ozone mixing ratio variation in the middle and upper stratosphere. The amplitude of the first (annual) harmonic was shown to be small in the subtropics but increased to a maximum at polar latitudes. The amplitude also increases with height in the middle and upper stratosphere to an apparent maximum just below the stratopause. The second (semi-annual) harmonic has an amplitude that is largest in tropical regions and in subpolar regions at a height of about 40 km.

The phase of the first harmonic shows a marked transition from a winter/spring maximum below 30 km to a summer maximum at 30 km, changing rapidly to a maximum in winter in each hemisphere.. The regions of minimum amplitude of the annual variation and the marked phase shifts with height both indicate the separation by levels of the dominant physical control mechanisms on the periodic changes of the ozone mixing ratio in the middle and upper stratosphere. Changes below 30 km respond primarily to dynamic influences in the lower stratosphere while above 30 km the periodic variations result mainly from photochemical processes. Above 40 km these variations are strongly temperature dependent.

Analysis of ground based and satellite derived total ozone also shows a strong QBO in tropical ozone that is coherent with the observed QBO in tropical zonal winds. In the tropics, the total ozone variation appears to be nearly in phase with the tropical zonal wind QBO. In the stratosphere, the observed amplitude of the ozone QBO is fairly small above about 30 km.

Long series of observed stratospheric mean monthly zonal winds and temperatures were analyzed for a number of stations in the tropics, and these data were used, in part, for input to a coupled photochemical/radiative/ dynamic model to reproduce the satellite observed (Nimbus-4) ozone QBO in the tropics. The calculated vertical variation of amplitude and phase of the oscillation agree quite well with the observations. The phase of the ozone QBO decreases (maximum ozone occurs earlier) with height. But at 27-28 km there is an abrupt phase shift of about 180^{o} At the upper layers (30-35 km) and lower layer ($\sim$22 km) the derived and observed QBO phases agree. In the upper layers (30-35 km), derived ozone and temperature variations are out-of-phase. Below 27 km they are in phase. This is also a result of the different dominant physical/photochemical mechanisms affecting ozone variations below (vertical motions) and above (photochemistry including negative temperature feedback) about 27-28 km.

In addition to the above, we continue to study the variations of solar irradiance data in the UV (120-310 nm) as processed from SME observations. The results of most interest to stratospheric modelers of possible upper air responses to short term solar variations is the range of solar irradiance observed during different solar rotation periods. This range, in general, decreases during the declining phase of the solar cycle. For Lyman-alpha the range varied from a maximum of 30% to as low as 6% in an 18 month period studied (6 December 1981 - 3 June 1983). The average range in the Schumann-Runge bands for the 20 solar rotations during this period is about 5% (not 15% as some have assumed). We will continue to study the spectral distribution of the UV solar irradiance derived from SME observations and incorporate these results in our theoretical modeling efforts.

Journal Publications:

London, J., Periodic and aperiodic ozone variations in the middle and upper stratosphere, Adv. Space Res., 2, 201-204, 1983.

Oltmans, S. J. and J. London, The quasi-biennial oscillation in atmospheric ozone, J. Geophys. Res., 87, 8981-8989, 1982.

Results of the ozone data analysis summarized here are included in a chapter entitled "The Observed Distribution of Atmospheric Ozone and Its Variations" as part of a book to be published this year by Van Nostrand and Co. (R. C. Whitten and S. S. Prasad, eds.).

The research reported here on the quasi-biennial oscillation of ozone and winds in the tropical stratosphere is part of a Ph.D. thesis being prepared by Xiu-de Ling, a graduate student in the Astro-Geophysics Department.

Title: Solar Maximum Mission Study of Mesospheric Ozone

Investigators: A. C. Aikin, Principal Investigator
J. R. Herman, Co-Investigator
Goddard Space Flight Center
Greenbelt, MD 20771

Research Objectives:

Mesospheric ozone is determined by measurement of the attenuation of solar ultraviolet radiation during twilight, using the Tanberg-Hanssen ultraviolet spectrometer polarimeter on the Solar Maximum Mission. These data are used in conjunction with other satellite data on composition and temperature structure to study the photochemical origin of mesospheric ozone and the influence of parameters such as water and temperature on the ozone distributions. In 1984 the measurement of mesospheric nitric oxide will be added in order to determine the vertical diffusion rate which best explains the data as well as the relationship of nitric oxide to ozone in the upper stratosphere.

Progress:

The ultraviolet spectrometer polarimeter on the Solar Maximum Mission has been used to measure ozone in the 50 to 70 km altitude region until data taking was interrupted due to satellite pointing failure. It is planned to repair the satellite during a two day extravehicular activity on Shuttle Mission STS-13 in April 1984. Analysis of data has shown a number of interesting features. Vertical profiles often exhibit a wavelike structure which may be associated with gravity waves. Comparison with a time dependent model shows that for the fall equinoctial period at the equator the vertical ozone distribution requires that the water vapor mixing ratio vary from 5 parts per million at 50 km to 2 parts per million at 65 km. In order to explain such a distribution it is necessary that the vertical eddy

Title: Solar Maximum Mission Study of Mesospheric Ozone
A. C. Aikin, Principal Investigator

Progress (con't)

diffusion coefficient have a value considerably less than the one usually associated with this altitude range. This result is in agreement with recent water vapor profiles deduced from ground-based water vapor microwave emission measurements.

Publications:

Aikin, A. C., B. Woodgate and H.J.P. Smith, Atmospheric ozone determination by solar occultation using the UV spectrometer on the Solar Maximum Mission, Applied Optics, 21, 2421-2424, 1982.

Aikin, A. C., B. Woodgate and H.J.P. Smith, Equatorial ozone profiles from the Solar Maximum Mission - A comparison with theory. Accepted for publication Planet. Space Sci., 1983.

Title: Analysis and Interpretation of the Nimbus-4 BUV and SCR Data

Principal Investigator: S. Chandra
Code 964
NASA/Goddard Space Flight Center
Greenbelt, MD 20771

Abstract of Research Objectives

The proposed research is for the study of the 7 years (1970-77) of the Nimbus-4 measurements of total ozone, ozone mixing ratio and temperature in the stratosphere. This study is being conducted with the following major objectives:

(1) Implications of radiative photochemical models on the seasonal variations of ozone and temperature, (2) possible relation between solar UV and ozone changes, and (3) short term perturbations of ozone and temperature fields and their relation to transient planetary waves.

Summary of Progress and Results

The total ozone and ozone mixing at various pressure levels in the stratosphere measured from Nimbus-4 BUV experiment over a 7-year period (1970-1977) have been used to study the possible effects of solar variability on stratospheric ozone. The study has shown that with the decrease in solar activity from 1970 to 1976, the globally averaged ozone inferred from Nimbus 4 data decreased from about 10-12 percent in the upper stratosphere to about 1-3 percent in the lower stratosphere. This systematic decrease at all pressure levels is modulated by a quasi-periodic oscillation of about a 2 year period. Both the systematic decrease and the quasi-periodic oscillations in ozone seem to be correlated with the conventional indices of solar activity suggesting a solar UV-ozone relationship. Despite this apparent correlation, it is difficult to account for the observed changes at various pressure levels with our current understanding of photochemical models and the solar UV flux variations over a solar cycle. The agreement between the observed and the calculated profiles of ozone mixing ratio is considerably improved if the BUV data is corrected for the changes in the instrument sensitivity using Umkehr observations as a reference.

A correlative study of ozone and temperature using 7 years of data has recently been undertaken to minimize certain subjectivities in correcting for the instrument sensitivity and to obtain a consistent picture of solar induced oscillations on different time scales. The study is providing interesting insights into our understanding of photochemical and dynamical processes controlling the ozone distribution in the stratosphere.

Publications

Chandra, S., A study of solar activity-ozone relationship from Nimbus-4 BUV data, "Solar Terrestrial Influence on Weather and Climate, 1983," ed. B. M. McCormac.

Chandra, S., An assessment of possible ozone-solar cycle relationship inferred from Nimbus-4 BUV data, J. Geophys. Res., in press.

Title: Stratospheric Satellite Data Analysis System

Investigators: Eugenia Kalnay, Wayman Baker (Laboratory for Atmospheric Sciences), and Marvin Geller (Laboratory for Planetary Atmospheres), Goddard Space Flight Center, NASA.

Research Objectives: To develop an interactive stratospheric/tropospheric analysis/forecast system in order to provide a four-dimensional analysis of the atmosphere during the FGGE Special Observing Periods 1 and 2. This analysis will include both directly observed fields such as temperature, geopotential height and horizontal wind, and diagnostic fields such as vertical velocities and heating rates derived through the use of the stratospheric/tropospheric GCM during the assimilation cycle.

Summary of progress and results: We made very good progress in the two main areas of development.

1) Model development:
The GLAS Fourth Order Global Atmospheric Model, originally developed for the troposphere, has been extended to include a well resolved stratosphere. This work, performed under the direction of Dr. M. Geller, included as principal changes: a) use of a hybrid vertical coordinate. In the troposphere the vertical coordinate is $\sigma = \frac{p-p_{INT}}{p_s-p_{INT}}$ between the surface p_s and a constant pressure p_{INT} = 120 mb, with 8 constant $\Delta\sigma$ levels. In the stratosphere the vertical coordinate is pressure, with 11 layers of constant $\Delta \ell n p$ (Fig. 1). b) Use of potential temperature as prognostic variable, and a new hydrostatic equation, which result in several advantages in terms of conservation properties. c) The introduction of a hybrid ERL/GLAS radiation routine for the stratosphere/troposphere.

The model is ready for production, and has been tested using initial conditions from the NMC temperature analysis, and geostrophic initial winds. The model was quite successful in predicting the wave number 1 stratospheric warming of January 1979 (Fig. 2) and gave a reasonable prediction of the February 1979 wave number 2 warming (Fig. 3). Further model development for the analysis cycle will include a new radiation scheme and suitable dissipation parameterization. An extensive documentation of the tropospheric model and stratospheric modifications is now available (Kalnay et al., 1983).

2) Analysis scheme and data collection:
Very good progress also took place in this area. A 2-dimensional multivariate optimal interpolation (O/I) analysis scheme, developed for tropospheric analysis, has been extended into the stratosphere for analysis of data on 18 mandatory pressure levels (Fig. 1). The analysis scheme has been coupled to the 19 level stratospheric/tropospheric model described before, and is currently being modified to use special stratospheric data sets such as LIMS and rocketsondes. Arrangements have been made with Dr. J. Gille to acquire the new, more accurate LIMS Version 5 data in the FGGE II-b format for use at Goddard and by the atmospheric research community.

During FY84 we plan to convert the analysis/forecast system to the Cyber 205, although it should be noted that additional Cyber memory will be necessary in order to run productively.

Reference: Kalnay, E., R. Balgovind, J. Edelmann, J. Pfaendtner, L. Takacs and W. Chao, 1983: Documentation of the GLAS Fourth Order General Circulation Model and its stratospheric extension. NASA Tech. Memo., in press.

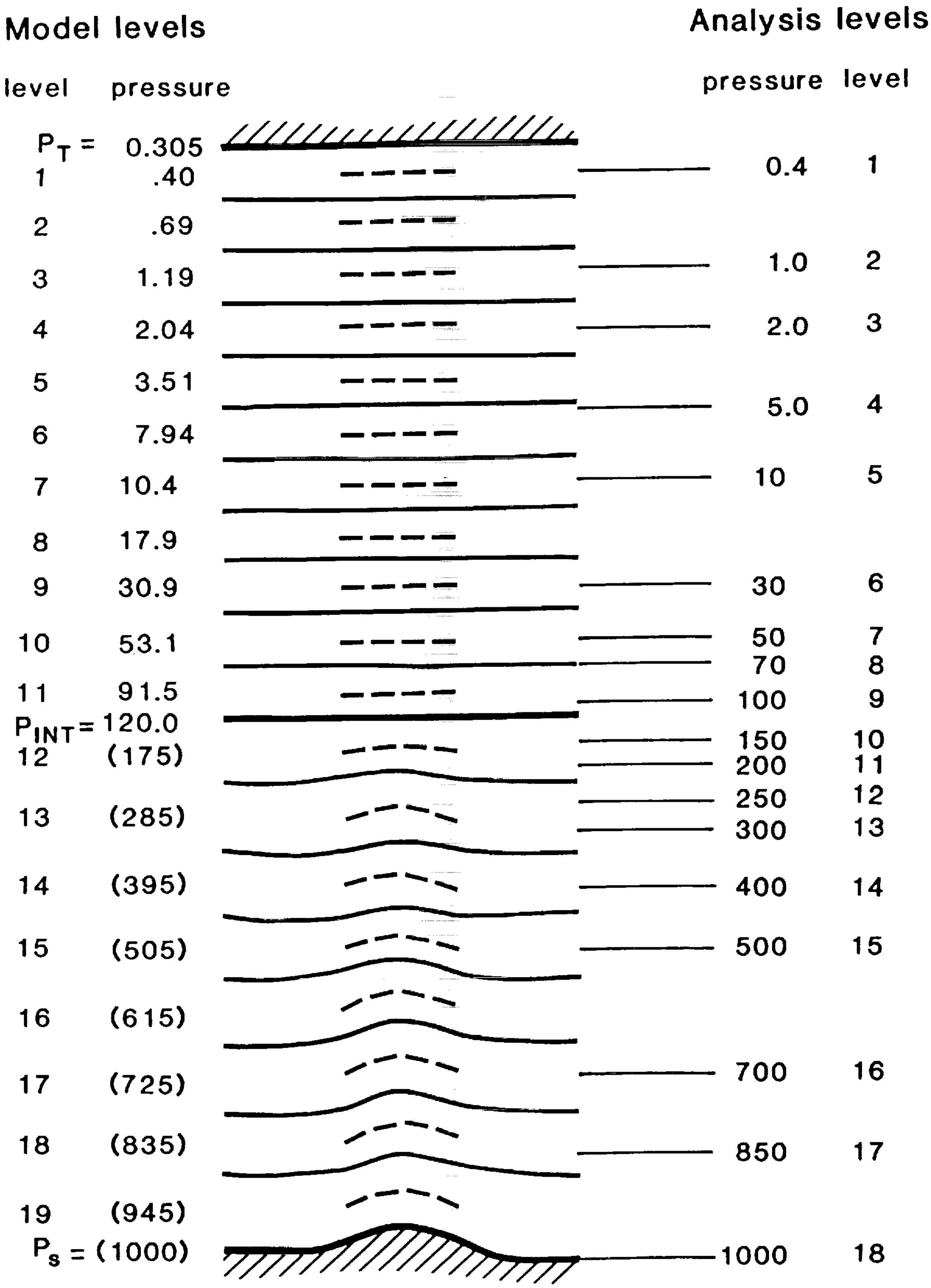


Fig. 1. Stratospheric/tropospheric model prognostic levels and mandatory pressure analysis levels. Note that model levels were chosen to minimize vertical interpolation between analysis and model.

Fig. 2. 5 mb geopoential heights

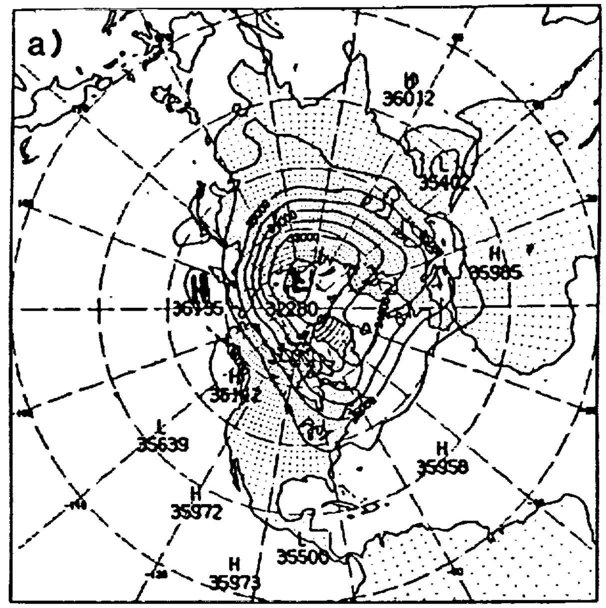
a) Initial conditions on 19 Jan 1979, 12z

b) 4-day forecast

c) Verification on 23 Jan 1979, 12z

d) 7-day forecast

e) Verification on 26 Jan 1979, 12z



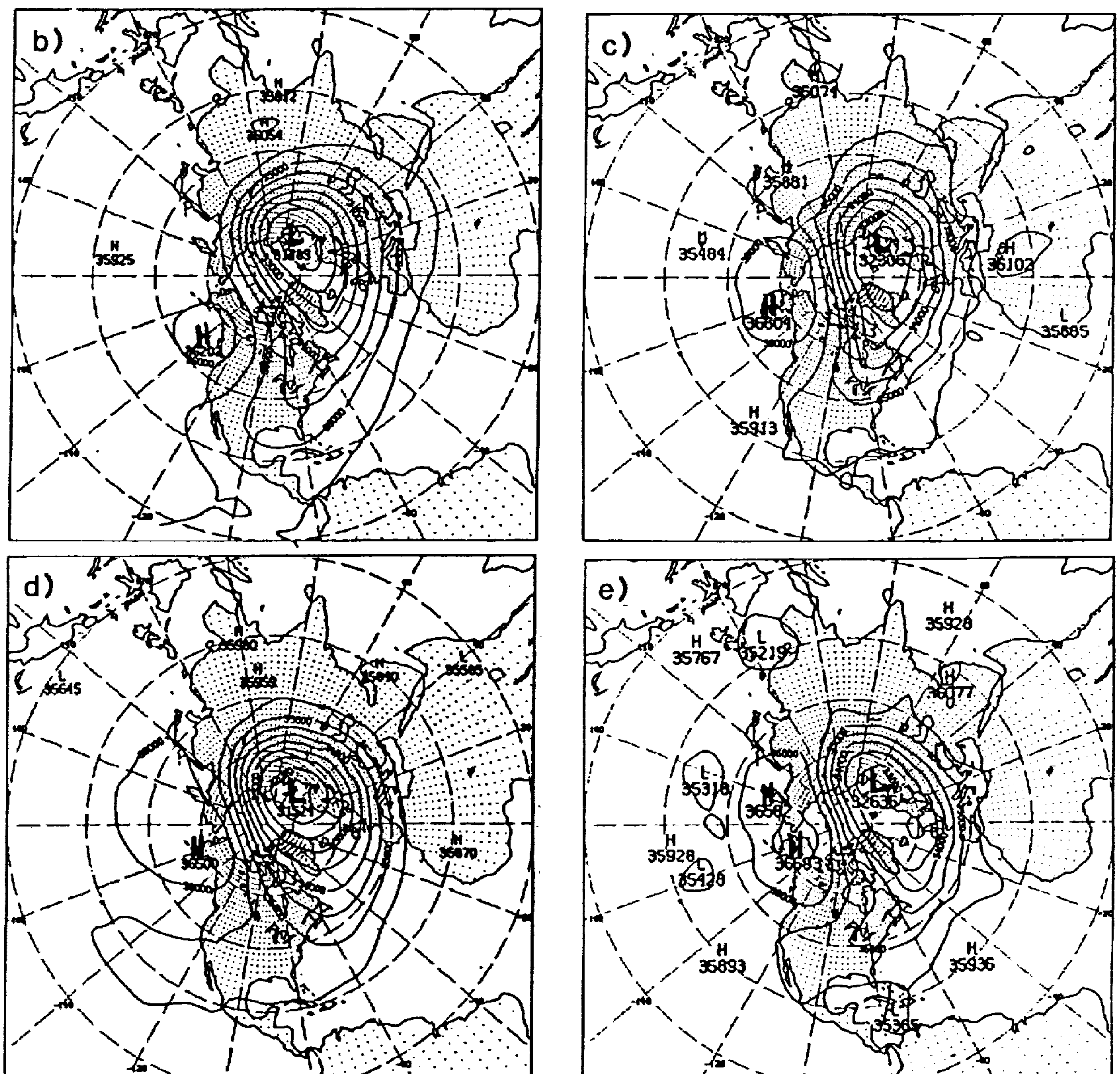


Fig. 3. 5 mb geopotential heights

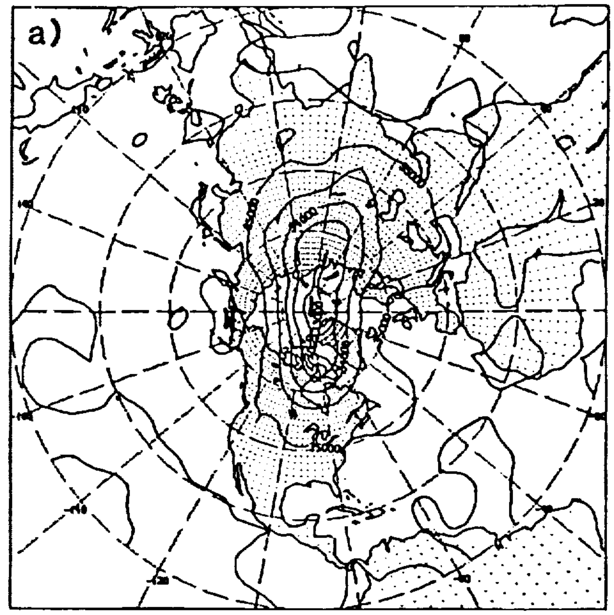
a) Initial conditions on 19 Feb 1979, 12z

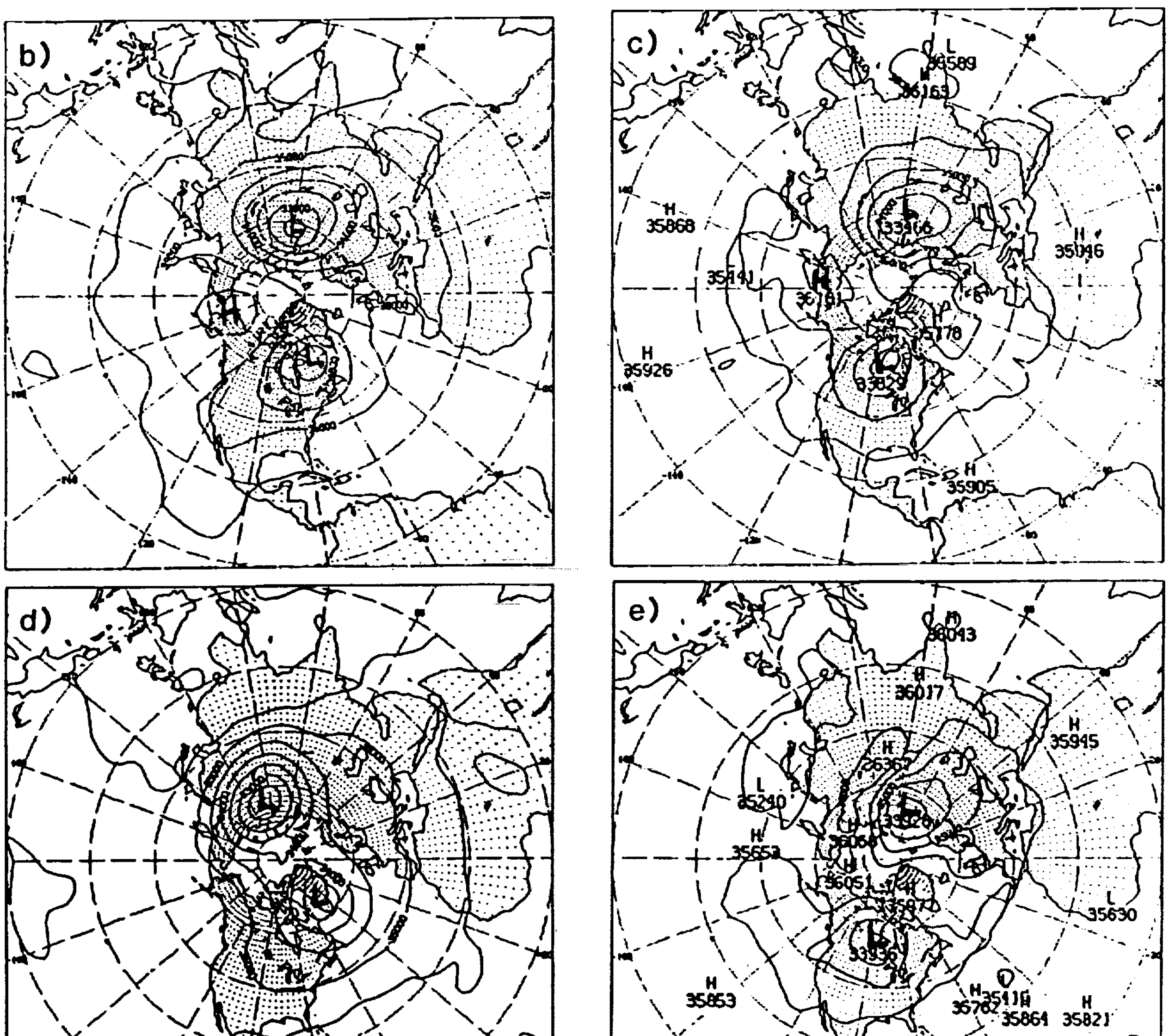
b) 3-day forecast

c) Verification on 22 Feb 1979, 12z

d) 6-day forecast

e) Verification on 25 Feb 1979, 12z





Title:

LIMS Storage and Evaluation

Investigators and Institutions:

Dr. James M. Russell III and Mr. Anthony Jalink Jr., NASA Langley Research Center

Abstract of Research Objectives:

The purpose of this effort is to maintain the LIMS engineering model (EM) in an enclosed, specially designed shipping container, to inventory all parts and test equipment and secure them, and to evaluate the work that would be required to make the LIMS EM flight ready. The intent is to eventually fly the EM on a shuttle, or more preferably on a long term mission to obtain more data of the type collected in the flight of the protoflight model on Nimbus 7. That experiment provided the most comprehensive data set ever collected on the upper atmosphere. Unfortunately, it only covered the Northern Hemisphere winter. A flight covering the summer and Southern Hemisphere winter is highly desirable to investigate phenomena that appeared to be developing there in the fall based on the Nimbus 7 flight. Also, the Northern Hemisphere summer data can be studied in relation to the Nimbus 7 results.

Progress and Results:

The LIMS EM is being stored in its specially designed shipping container in a temperature controlled room at Honeywell. The instrument was recently visually inspected and appears to be in good shape. There is a large amount of documentation also being maintained with the equipment. Contact has been made with personnel at the GSFC concerning the possibility of integrating the GSFC procured Phillips magnetic suspension refrigerator system with the LIMS. This would avoid mechanical environmental and safety questions associated with flying the LIMS solid cryogen on the shuttle. It would also provide a test application for the cooler and facilitate multiple reflights of the LIMS. As a minimum, the detector capsule assembly would have to be redesigned to accept the refrigerator cold sting. Honeywell would perform a study of changes, refurbishment activities, testing, and effort required to integrate the new cooler for about $150K.

A. Title of Research Task

Satellite MFR total ozone analyses.

B. Investigators and Institutions

J. Ellis, J. Lovill, F. Luther, T. Sullivan, R. Weichel
Lawrence Livermore National Laboratory
Livermore, California

C. Research Objectives

The objective of this research effort was to determine values of total ozone globally from the infrared radiance data from Multichannel Filter Radiometer (MFR) sensors onboard four DMSP satellites. These satellite sensors provided data from March 1977 to February 1980. The total ozone data provided by these sensors were to be intercompared with surface-based sensors measuring total ozone, and the data will be made available in a historical data archive.

D. Progress and Results

This project was completed in early 1983. This effort provided worldwide total ozone data for approximately 1000 satellite-days from March 1977 to February 1980. When the MFR satellite total ozone data were compared with Dobson spectrophotometer observatory total ozone data, it was seen that the Dobson data were approximately 5% greater than the MFR data. The MFR radiance data and total ozone data have been made available to the scientific community and are available from the National Space Science Data Center at NASA Goddard, Greenbelt, MD.

E. Journal Publications

Lovill, J., J. Ellis, F. Luther, T. Sullivan, R. Weichel, "Defense meteorological satellite measurements of total ozone," Geophys. Res. Lett., 9, 105-108, 1982.

Development of A Stratospheric Ozone and Meteorology Climatology from Satellite and Ground-based Observations

Principal Investigator:	Alvin J. Miller	NOAA/NMC/Climate Analysis Center
Co-Investigator:	Melvyn E. Gelman	NOAA/NMC/Climate Analysis Center
Co-Investigator:	Ronald M. Nagatani	NOAA/NMC/Climate Analysis Center
Co-Investigator:	Keith W. Johnson	NOAA/NMC/Climate Analysis Cetner

Investigators at Other Institutions

Dr. D. F. Heath	- Goddard Space Flight Center
Dr. A. J. Fleig	- Goddard Space Flight Center
Dr. M. Geller	- Goddard Space Flight Center
Dr. R. Stolarski	- Goddard Space Flight Center
Dr. J. Frederick	- Goddard Space Flight Center
Professor Karin Labitzke	- Free University of Berlin, FRG
Professor George Tiao	- University of Wisconsin
Professor Greg Reinsel	- University of Wisconsin
Dr. John Deluisis	- NOAA
Dr. Carl Mateer	- AES, Canada

Abstract

The objective of the proposed work-effort is to establish a climatology of the stratospheric total ozone, ozone mass mixing ratio (25-55 km) and meteorological parameters (height, temperature, wind) which will provide input data for a number of research programs and contribute to the basis for validating atmospheric models designed for numerical prediction of weather and climate. The elements of this program are as follows:

- Calculate the meteorological and ozone synoptic climatology with respect to major versus minor stratospheric warming events defined by the synoptic meteorological charts as well as by monthly average.

- Develop the distribution of the above parameters in wave-number space.

- Determine the temporal variations in above parameters including long-term trends and periodicities.

- Merge the meteorological and ozone data series to compute transports and ozone-temperature relationships. From such data, eddy difussion coefficients will be computed from comparison with current two-dimensional models.

Summary

Global fields of geopotential height and temperature at stratospheric levels 70, 50, 30, 10, 5, 2, 1 and 0.4 mb have been produced since September 1978. As both data sources and analysis procedures have changed through the period, more than 2500 rocketsonde/rawinsonde profiles have been assembled and compared with the analysis values. Results of these comparisons indicate that systematic differences as a function of latitude can occur that may be as large as $9^{o}C$. Root mean square temperature differences between the two measurements range from about $4^{o}C$ at 5 mb to about $7^{o}C$ at 0.4 mb. When the systematic adjustments are applied, the analyses can be used for studies of the stratospheic general circulation including year-to-year variations.

Monthly average Northern and Southern Hemisphere maps of total ozone derived from BUV for the period 1970-1976 have been archived on magnetic tape at NSSDC and published as a NASA Reference Publication. Similar maps for upper level retrievals at 30, 10, 5, 2 and 1 mb have been archived at NSSDC and publication is in progress. Daily and monthly average synoptic maps of total ozone as well as vertical profiles 30 to 0.4 mb for the first two years of SBUV data, November '78 - October '80, have been archived at NSSDC and we are in process of microfilming all products.

The trend in total ozone has been evaluated for the mid 70's utilizing the BUV and ground-based informaiton with no discernable trend detected. This is in agreement with current estimates for possible anthropogenic impact. In the case of upper level ozone variations, our principal effort, thus far, has been to examine the ground-based Umkehr data as these will be used to cross compare the BUV and SBUV data sets. After extensive analysis by the working group to include changes in instrument calibration and stratospheric aerosol loading, a trend from 1970-1980 of about -3.5% was detected which compares to recent model estimates of about -2.9% (see attached diagram). A paper is being prepared for publication and effort has begun on analysis of the satellite information.

Finally, we are in process of merging the meteorological and ozone synoptic analyses for the period November '78 - October '80 and are calculating ozone-temperature photochemical relationships as well as eddy transports and associated variations during sudden warming episodes.

Publications

Miller, A. J., R. M. Nagatani, T. G. Rogers, A. J. Fleig and D. F. Heath, 1982: Total ozone variations 1970-74 using Backscattered Ultraviolet (BUV) and ground-based observations. J. Appl. Met., 21, 621-630.

Heath, D. F., A. J. Fleig, A. J. Miller, T. G. Rogers, R. M. Nagatani, H. D. Bowman II, V. G. Kaveeshwar, K. F. Klenk, P. K. Bhartia and K. D. Lee, 1982: Ozone Climatology Series Vol. 1, Atlas of Total Ozone April 1970-December 1976. NASA Reference Publication 1098, 163 pp.

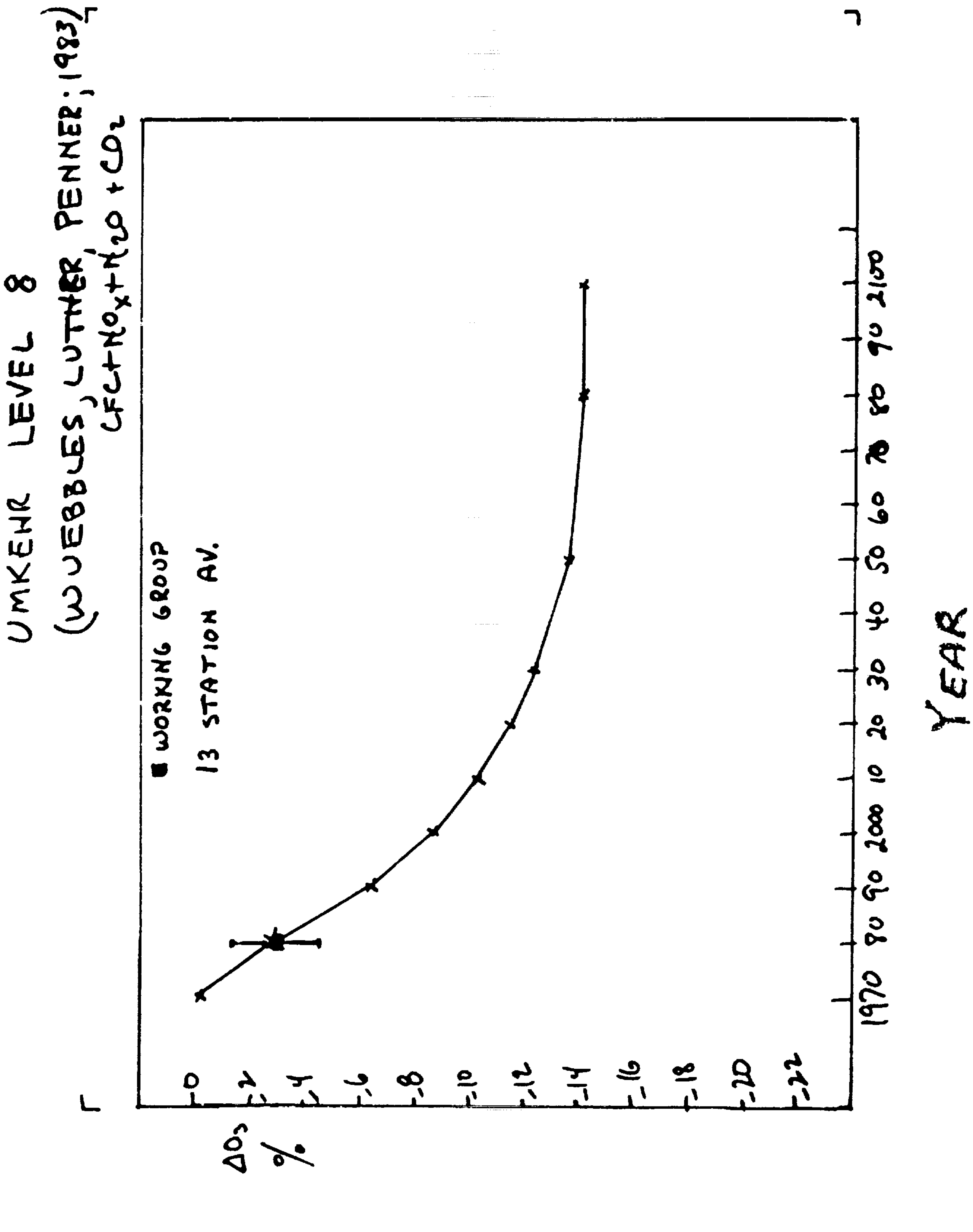
Gelman, M. E., R. M. Nagatani, A. J. Miller and H. D. Bowman II, 1983: Mean zonal wind and temperature structure during the PMP-1 winter period. Advances in Space Research, 2, 159-162.

Miller, A. J., R. M. Nagatani and M. E. Gelman, 1983: Meteorological influences on ozone distribution during the stratospheric warming of January-February 1979: Part II. Fourth Conference on the Meteorology of the Upper Atmosphere of the American Meteorological Society, March 22-25, Boston, MA.

Reinsel, G. C., G. C. Tiao, A. J. Miller, C. L. Mateer, J. Deluisi, and J. E. Frederick, 1983: Analysis of upper stratopsheric Umkehr ozone profile data for trends and the effects of stratospheric aerosols. Presented at Spring Meeting of the American Geophysical Union, Baltimore, MD.

Nagatani, R. M. and A. J. Miller, 1983: Stratospheric ozone changes during the the first year of SBUV observations - Novemver 1978-October 1979. To be published J. Geoph. Res.

Geller, M.A., M. Wu and M. E. Gelman, 1983: Troposphere-stratospheric monthly winter general circulation statistics for the Northern Hemisphere-four year averages. J. Atmos. Sci., 40, 1334-1352.


UMKEHR LEVEL 8
(WUEBBLES, LUTHER, PENNER; 1983)
CFC+NOx+N2O+CO2
WORKING GROUP
13 STATION AV.
ΔO3 %
YEAR
1970 80 90 2000 10 20 30 40 50 60 70 80 90 2100
0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22

RESEARCH SUMMARY

Title: Analysis of Selective Chopper Radiometer (SCR) Temperature Data, January 1975 - May 1978.

Investigators:

Jon Roe, Dale Hovland, and Robert Wilcox of the Meteorology Research Center of Control Data, Minneapolis, Minnesota.

Abstract:

The current tasks are to extend the retrieval of temperatures from the SCR instrument to the period January 1975 to May 1978, and also to prepare gridded values by careful space-time interpolation for that period. Temperatures are retrieved at 10, 5, 2, 1, and 0.4 mb at 4 degree latitude intervals along the orbit, from Nimbus 5 SCR-B radiances. The retrievals are based on regressions with meteorological rocket data.

Summary of Progress and Results:

All work on this contract has now been completed, except for the final report, which will be available shortly. Tapes containing data for 1975 - 1976 were delivered to GSFC approximately a year ago. Tapes containing orbital data from January 1977 - May 1978, and space-time interpolated values for the period January 1975 - May 1978, will be sent in September 1983, along with the final report. The data preparation under this task is basic research material useful for many stratospheric investigations. The data constitute a major resource for research efforts being undertaken here on the dynamic characteristics of observed sudden warmings.

Publications:

None.

SUMMARY OF RESEARCH TASK

A. Title: Empirical Stratospheric Model Development and Interpretation

B. Investigators and Institutions:

Principal Investigator: Gerald M. Keating, NASA Langley Res. Cen. (LaRC)
Hampton, VA 23665

Co-Investigators: John E. Nealy, NASA LaRC
James M. Russell III, NASA LaRC
Robert H. Tolson, NASA LaRC
John Y. Nicholson III, Systems and Applied Sciences Corp., NASA LaRC
J. J. Barnett, Oxford University, Oxford England
W. J. Borucki, NASA Ames Res. Cen., Moffett Field, CA
P. J. Crutzen, Max Planck Institute for Chemistry, Mainz, FRG
J. Pyle, Rutherford-Appleton Labs, Chilton, England

Others: Michael C. Pitts, Systems and Applied Sciences Corp., NASA LaRC
David F. Young, Systems and Applied Sciences Corp., NASA LaRC

C. Abstract of Research Objectives: The major emphasis in this continuing program is toward taking advantage of the global and complementary nature of the many data sets of stratospheric measurements recently obtained from satellites to obtain a detailed understanding of systematic variations in the stratosphere. The main objectives are to: (1) Develop empirical representation of data which will condense measurements of stratospheric trace species and temperature from a number of satellite experiments to a usable form, (2) study the nature and implications of a number of systematic variations detected from these data, and (3) develop Interim Reference Models of mean conditions, systematic variations, and long-term trends.

D. Summary of Progress and Results (F. Y. 1982-1983): Recently, emphasis has been on studying the response of ozone (O_3) to temperature (T) variations. These studies were performed to: (a) Identify areas of agreement and disagreement with contemporary photochemical theory, and (b) to isolate the variations of ozone associated with trace species variations and solar ultraviolet variations from those associated with temperature variations. Detailed studies have been performed by the authors concerning the relation between Nimbus 4 BUV ozone mixing ratios and SCR temperature data. The relationship between variations in zonal means of T and O_3 were investigated as well as the relationship between longitudinal variations in T and O_3. These studies were performed each month in 4° latitude increments at a number of pressure levels. It was found that positive correlations occurred between T and O_3 in the lower stratosphere, changing to negative correlations in the upper stratosphere. The region of transition between positive and negative correlations had substantial latitudinal-seasonal variations. The altitude of transition rises in areas of increased wave activity, including the winter hemisphere and high latitudes. The regression coefficient between variations in zonal means of O_3 and T in the upper stratosphere was studied in regions where the correlation coefficient exceeded -0.7. It was found that a region of maximum sensitivity of O_3 to T occurred near the stratopause. This "ridge" of maximum sensitivity of ozone to temperature variations was found to exhibit substantial latitudinal-seasonal variation. In winter, the ridge was found to rise with increasing latitude, while in summer it remained generally below 2 mb. Detailed comparisons were made with the recently updated Pyle et al. 2-D radiative-dynamical-photochemical model. Theory and observations showed excellent agreement in both the patterns of latitudinal-seasonal variations of the sensitivity ridge and the location of the regions of maximum sensitivities (near 2 mb in the Tropics and near 0.7 mb in winter high latitudes). However, the theoretical model indicated substantially lower sensitivities than the maximum values observed. A number of theoretical studies were performed on the effect of the $C\ell O_x$, NO_x, and HO_x families on the sensitivity of the O_3/T relationship using both the Pyle et al. model and the NASA Ames 2-D model. When all these families were removed, a sensitivity plateau occurred rather than a ridge. The principal chemistry controlling the sensitivity near the ridge appears to be that of the O_x and $C\ell O_x$ families. HO_x is only significant to sensitivities at altitudes considerably above the ridge and NO_x below the ridge. The difference between the observed and predicted sensitivity near the ridge would be reduced if: (a) The effect of $C\ell O_x$ on O_3 losses is substantially less than predicted, or (b) the temperature dependence of $C\ell O_x$ chemistry on ozone is much greater than generally assumed. In addition to improving predicted sensitivities, reduction of $C\ell O_x$ effects improves agreement between predicted and observed ridge altitudes.

Other accomplishments included: (a) Solar Physics review article published reviewing empirical and theoretical studies over the past 50 years of short-term and long-term solar activity relations; (b) reached agreement with Oxford University and Rutherford-Appleton Laboratories on collaborative empirical and theoretical studies of Nimbus 4 SCR, Nimbus 5 SCR, and Nimbus 7 SAMS data; (c) performed studies identifying mean distribution and systematic variations in O_3 as a function of pressure, latitude, longitude, solar activity, and time, and analyzed biases of satellite data from comparisons with ground-based and in situ data. These Interim Reference Models are being refined for possible inclusion in the COSPAR International Reference Atmosphere; (d) compiled essentially all airborne and ground-based stratospheric measurements of N_2O, NO, HNO_3, and NO_2 to be combined later with satellite measurements for data interpretation and generation of interim reference models; and (e) performed various auxiliary studies on ozone/temperature relationship, including effects of removal of long-term trends from data, nature of transition region between high positive and high negative correlations, empirical corrections for photolysis effects, and distribution of O_3/T sensitivities for long-term and short-term variations.

E. Bibliography (F. Y. 1982-1983)

Keating, G. M.: The Response of Ozone to Solar Activity Variations: A Review. Solar Physics, Vol. 74, No. 2, Dec. 1981, pp. 321-347.

Keating, G. M.; Lake, L. R.; Nicholson, J. Y. III; and Natarajan, M.: Global Ozone Long-Term Trends from Satellite Measurements and the Response to Solar Activity Variations. J. Geophys. Res., Vol. 86, No. C10, Oct. 20, 1981, pp. 9873-9880.

Keating, G. M.; Nicholson, J. Y. III; Young, D. F.; Pitts, M. C.; Barnett, J. J.; Nealy, J. E.; and Borucki, W. J.: Ozone Temperature Variations in the Upper Stratosphere. Presented at Ninth European Geophysical Society Meeting, University of Leeds, Leeds, England, Aug. 23-27, 1982. Abstract in Preprint Volume.

Keating, G. M.; Pyle, J. A.; Pitts, M. C.; Young, D. F.; Nicholson, J. Y. III; and Barnett, J. J.: Latitudinal-Seasonal Variations of Ozone-Temperature Relations. Submitted to 1983 Fall AGU Meeting, San Francisco, CA, Dec. 5-10, 1983. Abstract to appear in EOS, Trans. AGU.

Keating, G. M.; Pyle, J. A.; Pitts, M. C.; Young, D. F.; Nicholson, J. Y. III; Borucki, W. J.; and Barnett, J. J.: The Nature of the Response of Ozone to Temperature Variations in the Middle Atmosphere. To be submitted to J. Atmos. Chem., 1983

SUMMARY OF RESEARCH TASK

A. Title: DE-I Ozone Experiment

B. Investigators and Institutions:

Principal Investigator: Gerald M. Keating, NASA Langley Research Center (LaRC)
Hampton, VA 23665

Co-Investigators: Carlton L. Mateer, Atmospheric Environment Service (Canada)
Melvin A. Shapiro, National Center for Atmospheric Research (Colorado)
Pawan K. Bhartia, Systems and Applied Sciences Corp. (Maryland)
Kenneth F. Klenk, Systems and Applied Sciences Corp. (Maryland)
John Y. Nicholson III, Systems and Applied Sciences Corp. (NASA LaRC, Hampton, VA)
David F. Young (Systems and Applied Sciences Corp. (NASA LaRC)

Others: Walter E. Bressette - NASA LaRC
Alton P. Mayo - NASA LaRC
David Gordon - Systems and Applied Sciences Corp. (Maryland)
Lou A. Frank - University of Iowa, Iowa City, Iowa
John D. Craven - University of Iowa
Ted Peppin - University of Wyoming

C. Abstract of Research Objectives: To study the short-term temporal variations of synoptic and subsynoptic features of the field of total ozone by measuring backscattered ultraviolet radiation at two wavelengths (one which is attenuated by ozone and the other which is not) from a measuring platform 23,000 km above the Earth via the imaging instrumentation aboard the orbiting Dynamics Explorer I. With this Spin-Scan Ozone Imaging (SOI) Experiment, high resolution global-scale images are obtained in 12 minutes and an individual area can be studied many hours per day. Studies of these data should provide new insights into the nature of short-term spatial and temporal variations near the tropopause including the evolution of subsynoptic features, the evolution of the jet streams, the evolution of tropopause folding events, identification of possible precursors to severe storms, and a clearer understanding of the synoptic nature of the total ozone field. Objectives include measurement strategy, measurement scheduling, measurement validation, data reduction, and pilot studies of data analysis and interpretation.

D. Summary of Progress and Results (F. Y. 1982-1983): Detailed comparisons have been made between DE-I ozone images and ozone images obtained from the Total Ozone Measurement System (TOMS) aboard Nimbus 7. Considering the temporal variations which occur between the non-simultaneous observations, the agreements in both the observed cloud fields and ozone fields are striking. The spatial and temporal averaging of the DE-I data has been optimized, producing images with essentially the same character as the higher signal-to-noise ratio TOMS data. Using this optimum averaging to remove noise but preserve detail, the evolution of subsynoptic and synoptic features is clearly seen over intervals of less than 2 hours. These measurements of the short-term variations of the ozone field are unique. Since the launch of DE-I in 1981, the major effort has been toward measurement strategy, algorithm development, and validation. Measurement scheduling and strategies have been determined consistent with varying solar geometry and available opportunities. To date, data for approximately 10,000 ozone images (approximately 10,000 pixels each) have been collected on tape (approximately 100 million measurements). Approximately 10 million of these measurements (October 1981 data) are currently being reduced. Accomplishments to date include the following: (1) Obtained measurements over North America from morning to evening as well as measurements of other regions; (2) generated and validated preliminary pixel location software; (3) generated preliminary co-location software and performed preliminary validation; (4) generated preliminary scene reflectivity software and performed preliminary validation; (5) generated preliminary ozone determination software and performed preliminary validation comparisons between the SOI data and TOMS and Dobson data; (6) developed spherical harmonic, Fourier analysis, andother approaches for data analysis; (7) developed various imaging techniques for imaging ozone fields, cloud fields, and continental outlines on Earth grids for color stills and movies; (8) performed preliminary analysis of ozone fields with upper air parameters such as pressure fields, tropopause heights, jet streams, etc., and observed reasonable relationships; (9) incorporated a number of refinements in ozone algorithm; and (10) gave various contributed and invited papers, initial DE-I ozone paper is published, and another is essentially completed.

E. Bibliography

Keating, G. M.; Frank, L.; Craven, J.; Young, D.; Nicholson, J. III; Klenkm K.; and Bhartia, P.: Initial Ozone Measurements From the SOI Experiment Aboard Dynamics Explorer I. Presented at 1981 Fall AGU Meeting, San Francisco, CA, Dec. 7-11, 1981. Abstract in EOS, Trans. AGU, Vol. 62, No. 45, Nov. 10, 1981, p. 887 (Invited).

Keating, G. M.; Craven J. D.; and Frank, L. A.: The Field of Total Ozone as Observed with the DE Imaging Instrumentation. Presented at 1981 Fall AGU Meeting, San Francisco, CA, Dec. 7-11, 1981. Abstract in EOS, Trans. AGU, Vol. 62, No. 45, Nov. 10, 1981, p. 996.

Keating, G. M.; Frank, L. A.; Craven, J. D.; Young, D.; Nicholson, J. III; Bhartia, P.; and Gordon, D.: DE-I Total Ozone Measurements. Presented at 1982 Spring AGU Meeting, Philadelphia, PA, May 31 - June 4, 1982. Abstract in EOS, Trans. AGU, Vol. 63, No. 18, May 4, 1982, p. 386.

Keating, G. M.; Craven, J. D.; Frank, L. A.; Young, D. F.; Nicholson, J. Y. III; Bhartia, P. K.; and Bressette, W. E: Dynamics Explorer I Ozone Experiment. Presented at Ninth European Geophysical Society Meeting, University of Leeds, Leeds, England, Aug. 23-27, 1982. Abstract published in Preprint Volume.

Keating, G. M.; Frank, L.; Craven, J.; Shapiro, M.; Young, D.; and Bhartia P.: Global Pictures of the Ozone Field from High Altitudes from DE-I. Adv. Space Res., Vol. 2, No. 5, 1983, pp. 183-188.

Title of Research Task: TOMS Data Analysis

Investigators and Institutions:

Arlin J. Krueger — Goddard Space Flight Center

Melvyn A. Shapiro — National Oceanic and Atmospheric Administration

Abstract of Research Objectives:

The TOMS maps of global total ozone provide a unique view of the internal structure of the lower stratosphere and upper troposphere. This task is directed toward explaining the total ozone morphology in terms of dynamic and structural characteristics of the atmosphere. The end objectives are to understand the physical connection between transport and ozone variations and to use total ozone to infer atmospheric circulation.

A second research goal has been to explain excess absorption of ultraviolet light at the TOMS wavelengths in volcanic eruption clouds and to develop the means for quantitatively assessing the volume of sulfur dioxide from eruptions from the TOMS data. The objective includes the inference of chemical processes from the rate of change of sulfur dioxide.

Summary of Progress and Results:

TOMS data were analyzed in near real time in conjunction with meteorological field experiments in 1982 and 1983. Direct coordination with such experiments has been found necessary to obtain atmospheric data which are coincident with TOMS data and sufficiently detailed to be comparable to the TOMS resolution. The 1982 experiment was held in conjunction with the Alpex program, sponsored by NOAA and NSF, which was designed to determine the synoptic precursers to lee cyclogenesis in Southern Europe. The Nimbus orbits over Europe and the Atlantic Ocean were processed each day from February 22 until May 2, 1982 into ozone map form for delivery to the research aircraft operations center in France for use in flight planning. Additional orbits over North America were processed for studies of clear air turbulence in conjunction with Northwest Airlines. These orbits were instrumental in the discovery of a capability for measuring volcanic sulfur dioxide with TOMS because of the fortuitous eruptions of El Chichon in March - April 1982 while the ozone maps were being analyzed for the meteorological experiments.

In March 1983 the TOMS data were again processed in real time for use with special experiments conducted during the AGASP Program to examine the atmospheric structure associated with intense total ozone maxima found at high northern latitudes during the breakup of the polar night vortex. These ozone masses are characterized by very low tropopauses and cold temperatures. Two research aircraft flights in which the polar vortex ozone features were traversed were conducted during the program.

A principal analytical effort during this period was concerned with the measurement of volcanic sulfur dioxide with TOMS. It was demonstrated that excess absorption found at TOMS wavelengths over the El Chichon eruption cloud was due to sulfur dioxide rather than to carbon disulfide which also absorbs in the 310 nm spectral region. The spatial distribution of the sulfur dioxide can be readily obtained from the TOMS maps which are derived from spatially contiguous samples. This permits the measurement of the total mass of SO_2 produced during the eruption as well as the rate of change from day to day. These parameters could not previously be measured and were instead estimated from point samples. The importance of this development is that the ratio of oxidized to reduced sulfur in the plume can be determined, the chemical processes in the conversion of sulfur dioxide to sulfuric acid can be examined, and the climatic influence of volcanic aerosols can be quantitatively evaluated.

Journal Publications:

Krueger, A. J., (1983), Sighting of El Chichon sulfur dioxide clouds with the Nimbus 7 Total Ozone Mapping Spectrometer, Science, 220, 1377-1379.

A. Title of Research Task

A Medium Time-Period Modeling Effort of Solar Irradiance Variations in the Ultraviolet

B. Investigators and Institutions

Ludwig F. Oster
Joint Institute for Laboratory Astrophysics and Department of Astro-Geophysics, University of Colorado at Boulder, Boulder, CO 80309

C. Abstract of Research Objectives

A medium time-period (2 to 3 years) effort is proposed to improve significantly our predictive capability of irradiance variations of the sun in the ultraviolet. The elements of this proposal encompass a detailed study of existing ground-based observations and their possible improvements and of the requirements of individual (rocket) and short-term space-borne (statellites, space shuttle) calibration experiments, the definition of optimized parameters for irradiance predictions, and a long-term service program to provide data on ultraviolet irradiance for scientific and practial applications.

D. Summary of Progress and Results

A first step of the research task has been completed during the report period. This entails a detailed comparison between the several years of solar data in the EUV acquired by the AE-E satellite and ground-based comparison observations of solar active regions. The data channels used comprised hydrogen Lyman alpha and beta, the resonance lines of HeI and HeII, and FeXV lines. It was shown that the daily variations in the EUV and in solar radio emission (F10.7) correspond very closely to each other, but that the UV data are afflicted with serious and to date unrecognized calibration changes during the period of operation of the instruments. These changes appear to occur primarily after significant time lapses in data gathering and are easily recognizable as artifacts by plotting, for instance, ratios of Lyman alpha/beta intensities. Thus, it is not permissible to treat the entire set of data obtained between 1977 and 1980 as a block; rather, it must be separated into stretches with hopefully more or less uniform calibration.

This treatment has been subjected to a thorough statistical analysis and resulted in a recalibration. The now uniform data were then compared with daily measurements of the solar radio emission at 2800 MHz (F10.7) from the ground. Excellent agreement was found, leading to average ratios between the F10.7 flux and the EUV fluxes at the investigated wavelengths.

On the basis of these results we have concluded that there is at this time no evidence for the existence of a so-called slowly-varying background component in adddition to the excess emission (above the totally incative sun level) from individual active regions. This conclusion was corroborated by an investigation of the relationship between the FOV-restricted data from the AE-E satellite and the position of active regions on the sun.

As expected, there remain discrepancies between the EUV and the F10.7 levels for individual days which, for predictive purposes, limit the usefulness of statistical correlations. It is argued that the major cause is the single-parameter approach taken in this first analysis and that the primary candidate for a second parameter is the magnetic field configuration at and betwen individual active regions on the sun where the observed emission is originating.

Finally, in the framework of our first approach, typical levels of the solar irradiance in the EUV were derived for the periods of the activity maxima of cycles 20 and 21, and the intervening minimum (1970-1980).

E. Publication

Solar Irradiance Variations. 2. Analysis of the Extreme Ultraviolet Measurements Onboard the Atmosphere Explorer E Satellite. Journal of Geophysical Research, Paper 3A1207, in press (1983).

Ludwig Oster
25 August 1983

GRAPHIC HIGHLIGHTS: LEGENDS

Ludwig Oster
Solar Irradiance Variations

Figure 1. Sudden calibration changes of the EUV detectors onboard the AE-E satellite. Plotted is the measured Lyman beta intensity vs. Lyman alpha. The upper "scatter cloud" is solely occupied by data points from 1979; there were prolonged periods during which the equipment was not operational just prior to, and after, the data period. All other points are from the years 1976-78, and 1980.

Figure 2. Uniform set of corrected Lyman beta data. Shown are the raw data (circles represent individual measurements during operation gaps), the F10.7 ground-based measurements, and the recalibrated data based on our statistical analysis of EUV-F10.7 corrrelations.

Figure 3. The detection field (square) of the FOV-restricted monochromator sensitive to Lyman alpha, and the coverage of the solar disc by active regions (Ca+ K-line).

Figure 4. Comparison of FOV-restricted and full-disc data for a sample period in 1978. a. Monochromator (MN) 12, 6x6 arcmins, FOV-restricted. b. MN22, full disc, 60x60 arcmins. c. F10.7 intensities. d. Ca-K bright areas.

Figure 5. Expected EUV irradiance levels on the basis of our statistical analysis of EUV-10.7 correlations.

NOTE: The above numbering of figures is not identical to the one in the JGR publication

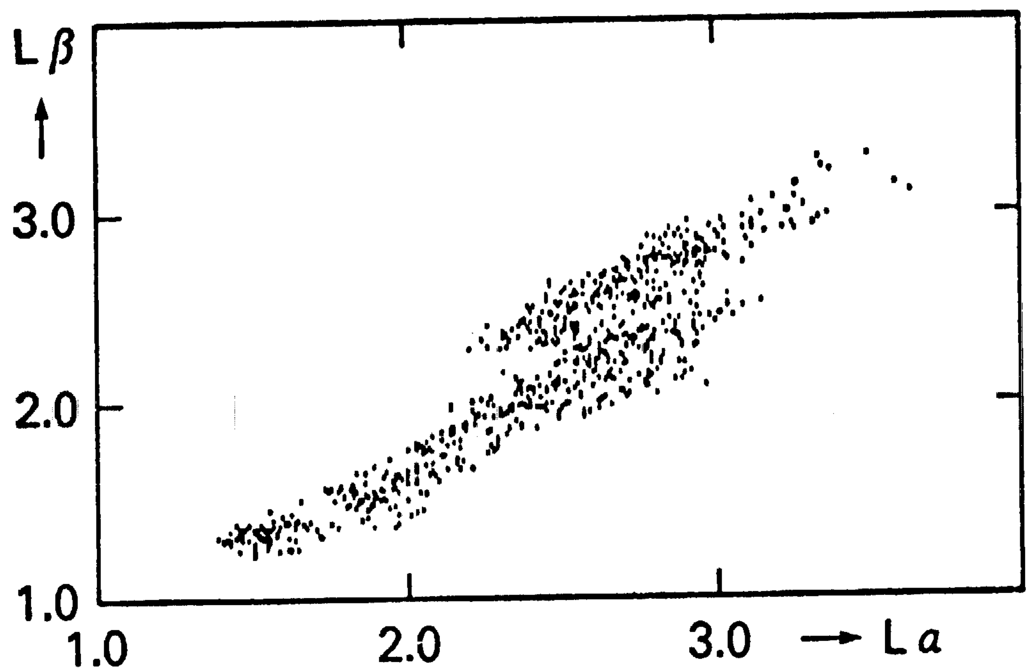
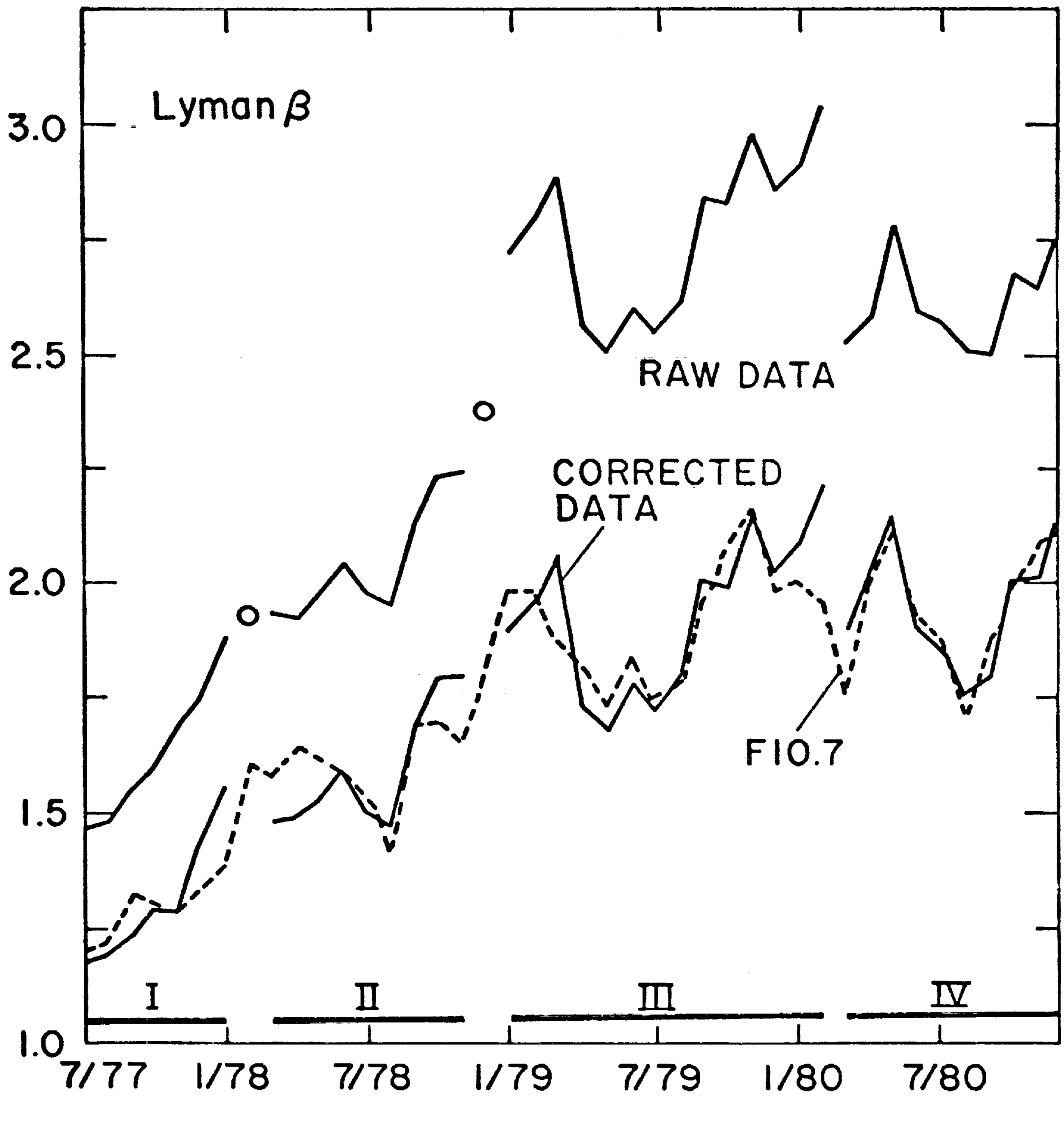


Figure #1



Lyman β
3.0
2.5
2.0
1.5
1.0
RAW DATA
CORRECTED
DATA
F10.7
I
II
III
IV
7/77
1/78
7/78
1/79
7/79
1/80
7/80

Figure 12

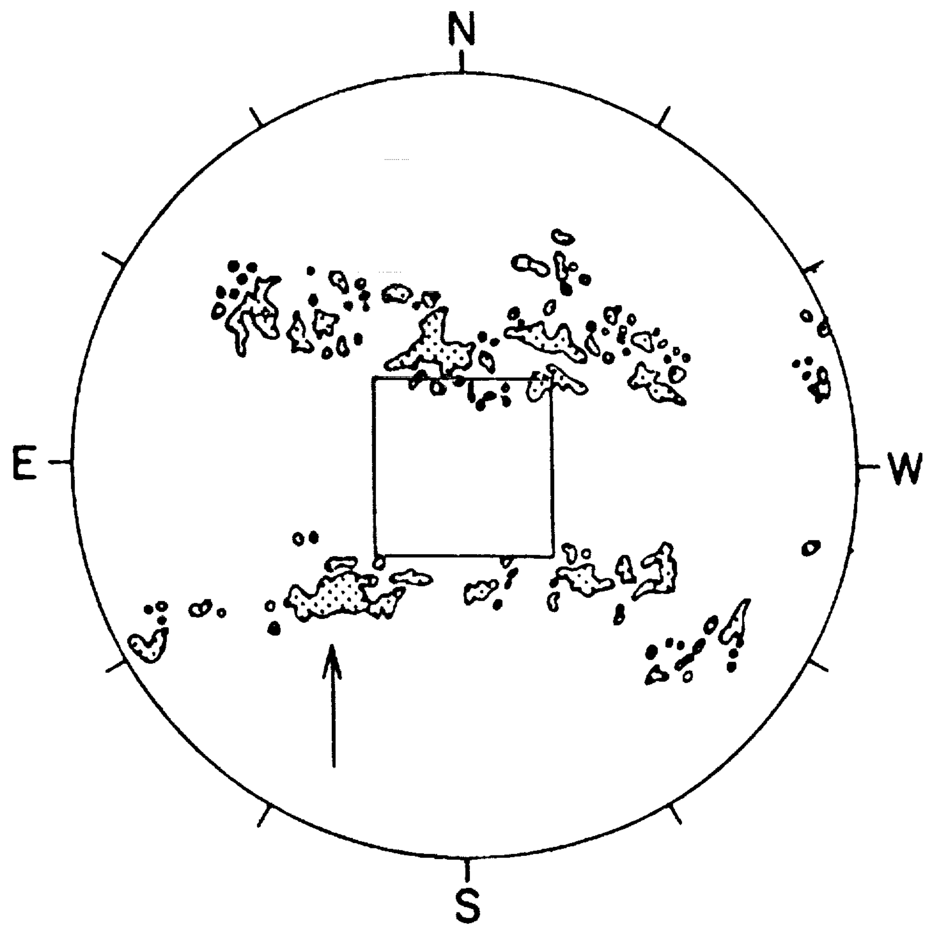


Figure ~~17~~3

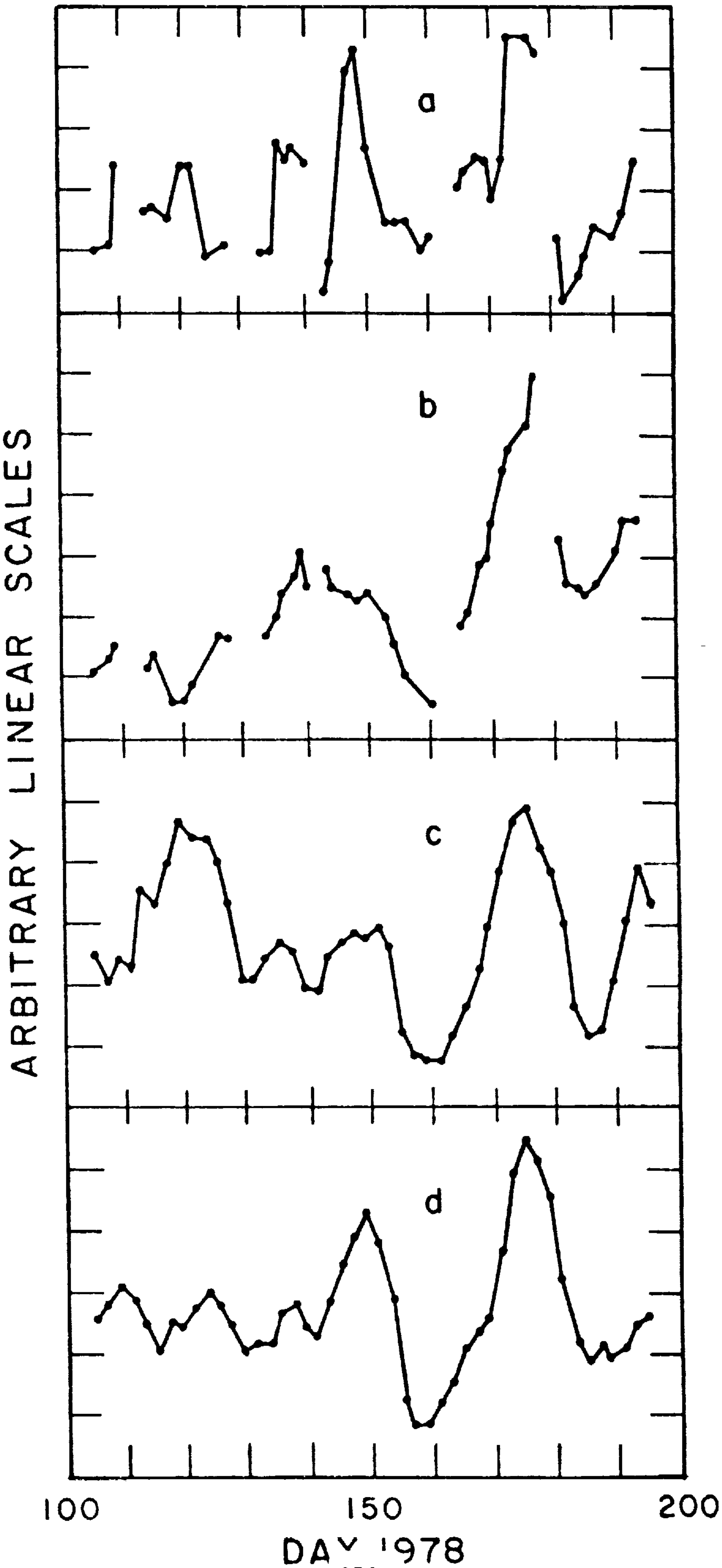


Figure ~~16~~ 4

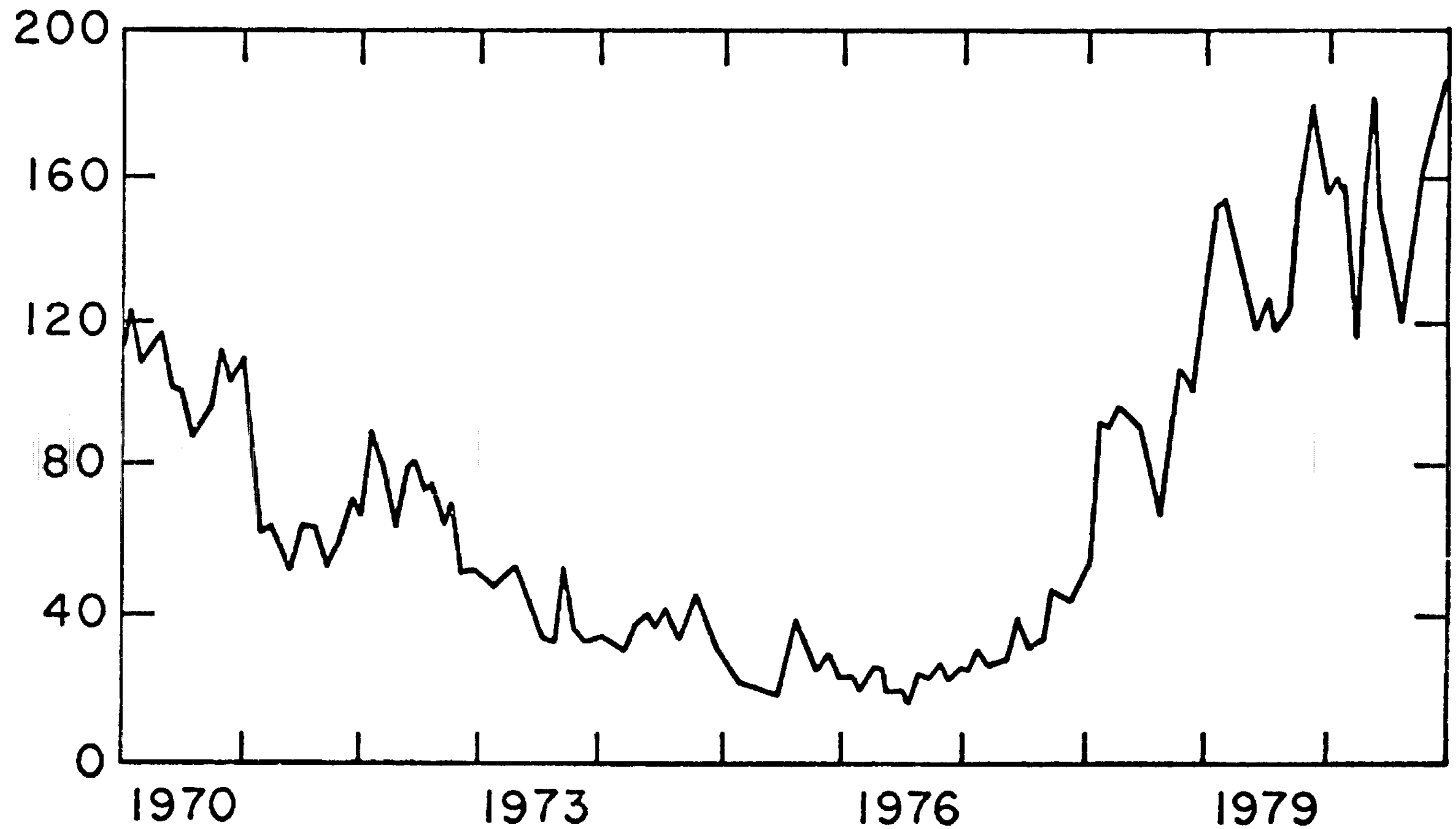


Figure ~~19~~5

Task II: Observations and Theories of O_3

Investigators: Dr. Y.L. Yung
Dr. M. Allen
Dr. L. Froidevaux
J. Lunine

Abstract of Research Objectives

Predictions of ozone depletion due to the increase in man-made trace gases such as the fluorochlorocarbons are an important part of stratospheric modeling, but have varied over the last decade, due in large part to changes in photochemical laboratory data. This research centers on the current ozone abundance, and existing observations are compared to photochemical models of the stratosphere and mesosphere. We attempt to understand and emphasize the existence of certain discrepancies which are ultimately relevant to a more exact prediction of ozone depletion.

Summary of Progress and Results

Although generally good agreement is found between our model and observations of HO_x, NO_x and ClO_x species that affect ozone in the stratosphre, the mean observed mid-latitude ozone abundance from about 35 to 50 km is up to 60% greater than model results. Given the current uncertainties in laboratory photochemical data, it is difficult to reconcile theory and observations by invoking such uncertainties; the model chemistry might be missing a significant ingredient. We point out the model ozone sensitivity to various parameters and suggeest that the $[O]/[O_3]$ ratio be remeasured in detail for comparison with theoretical expectations. Certain observations of a daytime increase in ozone near 40 km are also puzzling. Finally, the heavy ozone enhancement observed by K. Manersberger cannot be understood in terms of simple photochemistry (as we understand it at present), since fast isotopic exchange reactions between O and O_2 dominate the heavy odd oxygen system and will not allow any significant enrichment in heavy ozone.

A sizeable body of midlatitude mesosphere/lower thermosphere ozone measurements has been acquired within the last 15 years by a wide range of observing techniques. The variety of phenomena illustrated by these data sets can be explained by a simple photochemical model. The vertical distribution is well reproduced in model computations and its temporal variability can be understood as resulting from natural variability in environmental factors (temperature, water vapor, solar insolation). The abundance of ozone at the mesopause seems to undergo significant variation, which may abe the result of secular variation in the dynamics at that altitude range. Thus by chemical cycles involving oxygen and hydrogen atoms that are important in the stratosphere, but whose effects are hard to clearly isolate there, have been verified to a large degree in the simpler environment of the mesosphere.

Publications:

Allen, M., J.I. Lunine, and Y.L. Yung, The vertical distribution of ozone in the mesosphere and lower thermosphere, submitteed to J. Geophys. Res., 1983.

Froidevaux, L., M. Allen, and Y.L. Yung, manuscript in preparation, 1983.

Froidevaux, L., Ph.D. Thesis, Caltech, 1983.

RESEARCH SUMMARY

A. Title of Research Task: Stratospheric Circulation from Remotely Sensed Temperatures

B. Investigators and Institutions:

Dr. Lee S. Elson
Mail Stop 183-301
Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, CA 91109

C. Abstract of Research Objectives

In general terms, the objective of the proposed research is to develop an improved quantitative understanding of the large scale circulation of the lower stratosphere in the 15 to 30 km region. Higher stratospheric levels are strongly influenced by atmospheric tides which cannot be adequately accounted for using data from sun synchronous, polar orbiting satellites. This objective involves an evaluation of the improved vertical resolution of, and the use of winds deduced from satellite limb observations of temperature, and the identification and quantification of dynamical processes that are either second order but significant or first order but not included in conventional empirical analyses.

These general objectives can be divided into several parts. The impact of the higher resolution provided by limb soundings can be evaluated by comparing the results of conventional pseudo-geostrophic (PG) analyses using limb data sources with previous analyses using nadir data. This will be carried out for the zonally averaged circulation with emphasis on winter sudden warming events. In the equatorial regions, where waves are expected to have short vertical structure and small temperature amplitudes, the research will attempt to identify and quantify wave activity on a global scale.

Along with this assessment of the impact of the limb data set, an objective of this task is to evaluate the validity of the PG approximation on large scales (zonal wavenumbers 0-6), especially in equatorial and polar regions. Of particular interest are the sudden warming events. Important ageostrophic processes will be incorporated directly or through parameterizations into an improved empirical determination of the circulation as it affects heat, momentum and mass budgets. Where appropriate, limited sensitivity studies will be carried out.

D. Summary of Progress and Results

Work began on this task on April 1, 1983. Since that time, preliminary data tapes for a limited time period were obtained from the National Space Science Data Center. These tapes contained, in part, mapped geopotential fields deduced from data returned by the Limb Infrared Monitor of the Stratosphere (LIMS) instrument. Software routines have been developed which read the tapes and remove information of interest, reformatting the data for subsequent analysis. Additional routines have been developed which smooth and interpolate the data onto a height/latitude grid, performing numerical differentiation of both the zonally averaged and wave components of geopotential height. These differentiated products, along with the heights themselves, have been used to calculate the zonally averaged winds using the PG approximation. This calculation required the prior determination of momentum sources provided by the waves which was carried out by calculating the wave components of the wind using a pure geostrophic approximation, and then forming the appropriate zonally averaged correlations. Although the PG approximation only requires the calculation of the wave contribution to the zonal momentum equation, the often neglected meridional component was also calculated. In order to test the validity of the PG approximation, the calculated wind fields were then used to compare the size of the neglected terms with that of the included terms.

These calculations indicate that the superior vertical resolution of the LIMS instrument is likely to be the cause of disagreements between these results and previous results using nadir data. In most cases the differences are minor but significant, however a preliminary analysis of the wave forcing indicates that, during the intense period of sudden warming which was examined, the nadir and limb results differ by substantial amounts, and that the mean flow occasionally has significant departures from geostrophy. This departure is the result of the extremely large meridional acceleration caused by the waves in the polar regions. The preliminary analysis also indicates larger departures from geostrophy in the equatorial regions than previously reported.

E. Journal Publications: No publications have resulted from the first four months of this research effort.

SATELLITE DATA INTERPRETATION: CHEMISTRY AND TRANSPORT OF N_2O AND NO

Sheo S. Prasad[1], D. J. McLeese[1], D. J. Gorney[2], R. D. McPeters[3], L. A. Capone[4] and R. C. Whitten[5]

1. Jet Propulsion Laboratory, California Institute of Technology, Pasadena.
2. The Aerospace Corporation, Los Angeles.
3. Goddard Space Flight Center, Greenbelt, Maryland.
4. San Jose State University, San Jose, California.
5. Ames Research Center, Moffett Field, California.

Abstract of Research Objectives: Global observations of nitrous oxide in 20-50 km height range by the Stratospheric and Mesospheric Sounder experiment on board Nimbus 7 will be analyzed to elucidate atmospheric sources of this species. Mesospheric column content of nitric oxide from the SBUV experiment, and solar proton and electron precipitation measurements from IMP, S3-2 and DMSP satellites will be analyzed to study the flow of nitric oxide from its solar-terrestrial source region in the high latitude mesosphere.

Summary of Progress and Results: This research task was initiated only recently--near about mid-1983. We have now completed several improvements in Ames' 2D transport-kinetic model in order to use it for satellite data interpretation. We have also been able to increase our interaction with the Oxford University group regarding the understanding and use of their nitrous oxide measurements. Our first look at the latitudinal cross section of the monthly mean of N_2O mixing ratios suggests the possibility of atmospheric sources of this species driven by solar radiation. We are examining this possibility. However, due to the recent beginning of the research task, we do not have any specific result to report at this time.

Journal Publication: Due to the reason stated earlier, we do not have any journal publication to report.

Title:

Investigation of Upper Atmosphere Photochemistry, Dynamics, and Transport Phenomena Using LIMS Data

Investigators and Institutions:

Dr. James M. Russell III, Dr. William E. Grose, Dr. Ellis E. Remsberg, Linwood B. Callis, Kenneth V. Haggard, NASA Langley Research Center, and Larry L. Gordley, Systems and Applied Sciences Corporation.

Abstract of Research Objectives:

The objective of this research is to conduct scientific investigations of chemical and dynamical processes of the upper atmosphere using Nimbus 7 LIMS data. In the course of these studies, we will also use data from the SAGE program and other Nimbus 7 experiments (e.g., SAMS and solar irradiance data from SBUV/TOMS). The emphasis of the research is on identification of upper atmosphere phenomena revealed by the data, and on comparison of these observations with a 1-D photochemical model and a 3-D spectral, primitive equation, circulation/transport model. The first year's effort is being devoted to calculation of dynamical quantities, general chemical consistency checks between LIMS data and model results, development of a climatology for constituents and temperature, and diurnal change studies. Studies of constituent-temperature correlations, nitric acid transport, and NO_2 variability will be initiated. These latter studies will be completed in the second year and investigations of the water vapor budget and the major stratospheric warming of 1979 will be started. In the third year we will complete studies of the water vapor budget and the stratospheric warming, and initiate investigation of correlations between LIMS data, solar variability, and other processes.

Summary of Progress and Results:

One of the most interesting phenomena of the winter distribution of stratospheric NO_2 is the occurrence at times of very sharp latitudinal gradients with increasing north latitudes. In the literature this has sometimes been referred to as an NO_2 "cliff." We have examined these gradients using LIMS data, and we have made comparisons with theory using a photochemical model applied along trajectories on a constant pressure surface. The objective was to determine those transport and chemical processes which could support the LIMS observations. Fig. 1 shows comparisons of model results and LIMS data for the 10 mb level. Note the good agreement. Our conclusions, like those of Solomon and Garcia (1983), are that the gradient is consistent with the conversion of NO_2 to N_2O_5 at high latitudes and that the steep latitudinal slopes occur as a result of interaction between transport and photochemistry.

We have also studied the latitudinal variability of upper stratospheric and mesospheric NO_2 in the polar night region to evaluate the suggestions from theory that this region can be an NO_x source for the stratosphere. We have evaluated weekly zonal mean profiles measured over the periods December 1-5, January 5-9, and January 19-23. Fig. 2 shows the zonal mean latitudinal cross section for the period January 5-9. Note that as the boundary of the polar night is crossed (≈ 73°N), the NO_2 in the mesosphere sharply increases with altitude reaching ≈ 70 ppbv at ≈ 70 km. The results for the three periods together show a clear picture of the polar night mesosphere as a source for stratospheric NO_x.

Another study, concerning diurnal change in ozone, is in an early stage but some preliminary results are available. Fig. 3 shows the ozone profile in the polar night region starting at the tropopause (≈ 200 mb) and extending to about 75 km (≈ 0.02 mb). The profile reveals the presence of a second peak at about 70 km which is believed to occur because of advection of atomic oxygen from sunlit regions into the polar night. The subsidence accompanying the normal winter circulation leads to O_3 production by the three body reaction.

JOURNAL PUBLICATIONS

Accepted

Validation of Nitrogen Dioxide Results Measured by the LIMB Infrared Monitor of the Stratosphere (LIMS) Experiment on Nimbus 7, J. M. Russell III, J. C. Gille, E. E. Remsberg, L. L. Gordley, P. L. Bailey, S. R. Drayson, H. Fischer, A. Girard, J. E. Harries, and W. F. J. Evans, JGR, 1983

Examination of Wintertime Latitudinal Gradients in Stratospheric NO_2 Using Theory and LIMS Observations, L. B. Callis, J. M. Russell III, M. Natarajan, and K. V. Haggard, JGR, 1983

Validation of Water Vapor Results Measured by the LIMB Infrared Monitor of the Stratosphere (LIMS) Experiment on Nimbus 7, J. M. Russell III, J. C. Gille, E. E. Remsberg, L. L. Gordley, P. L. Bailey, H. Fischer, A. Girard, S. R. Drayson, W. F. J. Evans, J. E. Harries, JGR, 1983

Submitted

The Variability of Stratospheric and Mesospheric NO_2 in the Polar Winter Night Observed by LIMS, J. M. Russell, L. L. Gordley, E. E. Remsberg, S. Solomon, L. B. Callis, JGR, 1983

Spectroscopy and Transmittances for the LIMS Experiment, S. R. Drayson, P. L. Bailey, H. Fischer, J. C. Gille, A. Girard, L. L. Gordley, J. E. Harries, W. G. Planet, E. E. Remsberg, and J. M. Russell III, JGR, 1983

The Limb Infrared Monitor of the Stratosphere (LIMS): Experiment Description, Performance and Results, J. C. Gille, and J. M. Russell III, JGR, 1983

The Validation of Nimbus 7 LIMS Measurements of Ozone, E. E. Remsberg, J. M. Russell III, J. C. Gille, L. L. Gordley, P. L. Bailey, W. Planet, and J. E. Harries, JGR, 1982

Validation of Temperature Retrievals Obtained by the Limb Infrared Monitor of the Stratosphere (LIMS) Experiment on Nimbus 7, J. C. Gille, J. M. Russell III, P. L. Bailey, L. Gordley, J. H. Lienesch, W. P. Planet, L. V. Lyjak, and F. B. House, JGR, 1982

Accuracy and Precision of the Nitric Acid Concentration Determined by the Limb Infrared Monitor of the Stratosphere (LIMS) Experiment on Nimbus 7, J. C. Gille, J. M. Russell III, P. L. Bailey, E. E. Remsberg, L. L. Gordley, W. E. F. Evans, H. Fischer, A. Girard, and J. E. Harries, JGR, 1982

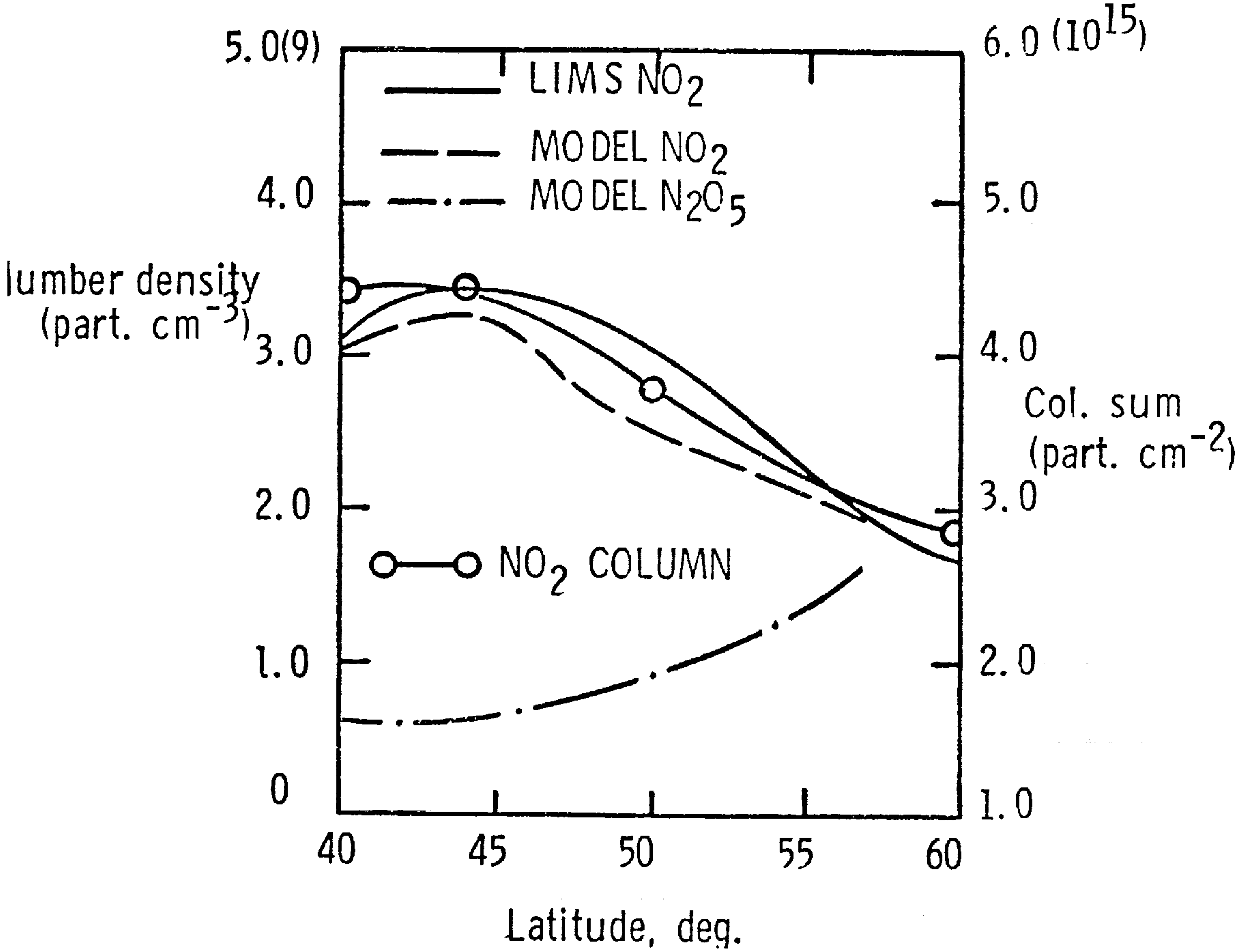


FIG. 1 COMPARISON OF OBSERVED NO_2 NUMBER DENSITY AND COLUMN AMOUNT (ABOVE 30 MB) WITH CALCULATED NO_2 AND N_2O_5 NUMBER DENSITY. (--) LIMS NUMBER DENSITY (O—O), LIMS COLUMN AMOUNT, (---) MODEL NUMBER DENSITY, (-•-•-), MODEL N_2O_5

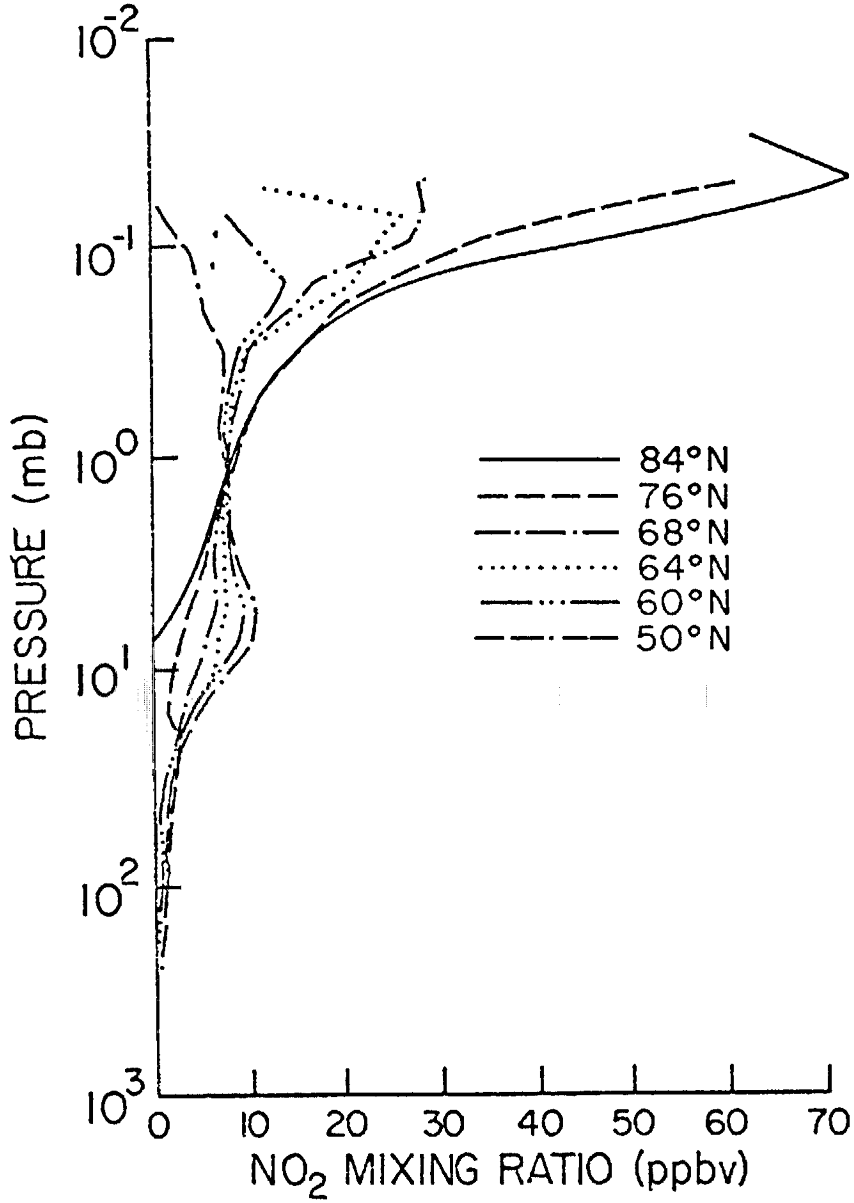


FIG. 2 LIMS ZONAL MEAN RADIANCE AVERAGED NIGHTTIME NO_2 RESULTS FOR JANUARY 5-9, 1979

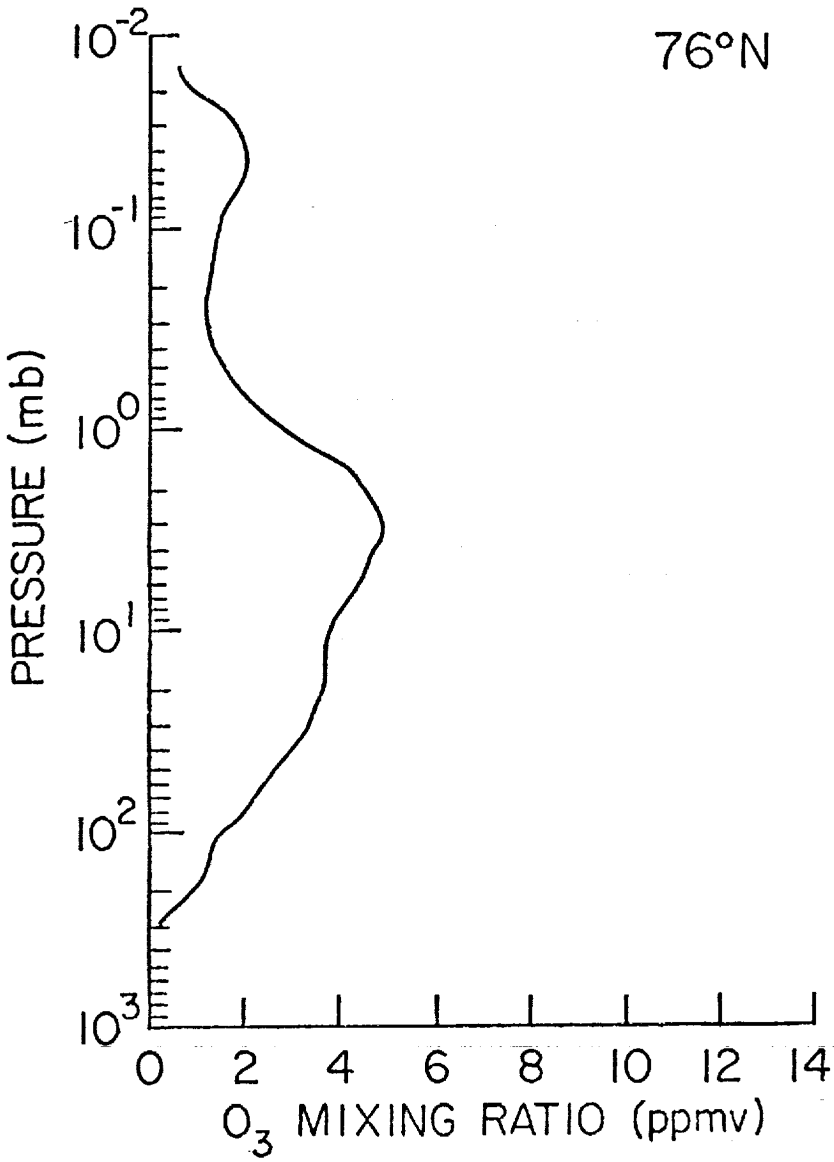


FIG. 3 PRESSURE VERSUS POLAR NIGHT OZONE MIXING RATIO OBSERVED BY LIMS AT 76° N USING RADIANCE AVERAGING FOR 240° E-360° E AND THE PERIOD DECEMBER 1-5, 1978.

Interpretation of NIMBUS-7 and SAGE-1 aerosol and trace gas data using three-dimensional models

P.I.: Professor R.G. Prinn, MIT, Cambridge, MA

OBJECTIVES: Utilize an efficient 3-D spectral model of the global troposphere and stratosphere with prescribed circulation to interpret trace gas and aerosol data from NIMBUS-7 (SAMS, SAM II, LIMS), SAGE-1, SME, and relevant in situ and ground-based instruments. Important initial goals include a determination of the global stratospheric sulfur budget and elucidation of the processes determining the spatial and temporal variations of sulfuric acid aerosols. Use of a 2-D model with a pre-calculated residual-mean circulation may also be explored.

SUMMARY OF 1983 PROGRESS: This project began in April, 1983. We have started by further validating the prescribed circulation in the 3-D model through additional detailed comparisons of predictions of the model with global observations of N_2O, $CFCl_3$, CF_2Cl_2, CH_3CCl_3, and CCl_4. Predictions and observations agree remarkably well and a paper by Golombek and Prinn entitled "A global three-dimensional model of the Circulation and Chemistry of $CFCl_3$, CF_2Cl_2, CH_3CCl_3, CCl_4, and N_2O" is being submitted to Tellus. In addition we have added the known sources (presently poorly defined) and chemical sinks (photolysis, reaction with OH, O) of OCS to the model - OCS is presumably the major source gas for stratospheric sulfuric acid when volcanic activity is low. We believe that we can assess the distribution of OCS sources from the OCS latitudinal distributions and are working on this possibility. The model is presently being transferred to the NASA-GSFC Cyber 205 computer--since this is proving to be a difficult process, progress will not be as rapid as we had hoped.

RESEARCH SUMMARY

Title: Dynamic Characteristics of Observed Sudden Warmings

Investigators:

Denis Dartt and Dave Venne of the Meteorology Research Center of Control Data, Minneapolis, Minnesota.

Abstract:

Our research goal is to understand the planetary wave dynamics of winter stratospheric sudden warmings by analyzing the evolution of a large number of events over a considerable depth of the atmosphere, 850 to 0.4 mb. This will require an analysis of large-scale stationary and transient planetary wave behavior using such diagnostic parameters as Eliassen-Palm fluxes and the index of refraction squared based on the zonal wind profile. Emphasis will be placed on interpreting the role of transient planetary waves in warmings and on determining those atmospheric features which encourage or inhibit warmings. Results will be examined for consistent characteristics that can be used to help improve current theories and models.

Progress:

The primary effort(beginning May 15, 1983) has involved programming and testing algorithms to diagnose planetary wave propagation characteristics and the interaction of these waves with the zonally averaged westerly flow. These programs provide planetary wave diagnostics in terms of the "transformed Eulerian-mean" framework and include the computation and display of Eliassen-Palm flux, the wave induced acceleration of the zonal flow, and the residual meridional and vertical circulation produced by wave transience. The primary input data to these programs are the latitude-altitude distribution of momentum fluxes and sensible heat fluxes for various waves on a daily basis. These programs provide a means of understanding the dynamics of warmings and will hopefully help us uncover some of the critical initial parameters when many such events are analyzed.

An initial effort has also been made to develop filters for isolating major traveling waves that may exist during the warming process, and also, to ready time series of wavenumber sin and cosine coefficients for application of these filters. Sensible heat and momentum fluxes by individual traveling waves can be isolated and analyzed dynamically within the "transformed Eulerian-mean" framework to underatand their effect on the warming process.

Publications:

None

SUMMARY OF RESEARCH TASK

A. Title: Analysis of the Stratospheric Global Diurnal Variations of HNO_3 and NO_2

B. Investigators and Institutions: Dr. Alton P. Mayo, Principal Investigator
NASA Langley Research Center
Hampton, VA 23665

C. Abstract of Research Objectives: The stratospheric nitrogen cycle is a major natural destructive cycle acting on the Earth's ozone layer. The source for the stratospheric nitrogen molecules is the N_2O diffused upward from the Earth's surface. The sink is HNO_3 which is transported down into the troposphere and rained out. The main constituents of the nitrogen cycle were measured by instruments on the Nimbus 7 spacecraft, covering the global region from 64°south latitude to 84° north daily, for the period from October 1978 thorugh May 1979. The research will analyze the global diurnal variations (night-day differences) of HNO_3 and NO_2 in the stratosphere by using available altitude profiles of these species as retrieved from the radiance measurements of the Limb Infrared Monitor of the Stratosphere (LIMS) instrument aboard the Nimbus 7 satellite. The effects of latitude, season, length of daylight, temperature, solar zenith angles, and global-scale stratospheric flow patterns on the species mean diurnal variations will be analyzed. The diurnal variations in the vicinity of the Noxon NO_2 cliff and the variations during the long polar day-night cycle will be studied. The adequacy of the photochemical theory to predict the diurnal variations will be illustrated by comparing the measured diurnal variations with the published theoretical results.

D. Summary of Progress and Results: The NO_2 and HNO_3 diurnal variations at a few selected data intervals at different seasons, length of day, solar zenith angle, and temperature have been obtained. Preliminary zonal distributions of the mean diurnal variations have been obtained for data intervals of up to 28 days surrounding the 1979 spring equinox, up to 7 days near the 1978 winter solstice, and for 4 days during May 1979. The zonal diurnal variations were determined at 15 selected latitudes and 10 altitude pressure levels. The diurnal variation global distributions were obtained using global sectors of 10° latitude by 10° or 15° longitude for profile averaging. The NO_2 and HNO_3 mixing ratio profiles were averaged over latitude zones and global sectors for both the front side (sunlit side) and back side (night side) of the Earth. These front side and back side average profiles were then differenced to obtain the mean diurnal variation (night-day difference).

The differencing of average night and day species profiles produces a spatial and temporal mean diurnal variation for an area. Alternately, where two orbit ground tracks (measurement tracks) cross, differencing the two profiles interpolated to the intersection point directly yields the diurnal variation at a specific time and global location. Limited initial results for this direct determination of the diurnal variations (using ground track intersection) have been obtained.

The primary effort up to the present has been to establish the software and obtain preliminary information on the diurnal variations. These preliminary results illustrate that, at some altitudes, the NO_2 mean zonal diurnal variation may be accurately determined from several days of data. The accuracies were determined solely by assuming random variation in the data sample and did not consider systematic errors. The measured NO_2 diurnal variation at the spring equinox and at 30° north latitude is in general agreement with the 1-D theoretical diurnal variations of Crutzen et al. (J. Geophys. Res., Vol. 83, No. Cl, Jan. 20, 1978, pp. 345-363) for 30°N and the fall equinox. The maximum theoretical HNO_3 mixing ratio diurnal variation obtained by Crutzen was about 0.10 to 0.20 parts per billion at approximately the 3 millibar pressure altitude. At the spring equinox, the maximum value of the measured HNO_3 mixing ratio diurnal variation is several tenths of a part per billion or 10 - 15 percent of the HNO_3 at the 7 millibar pressure altitude. Statistically, the standard deviation of the experimental HNO_3 diurnal variation is generally about 1 to 5 times the mean diurnal variation, depending on the altitude. At this effective assumed random variation level, it requires a few weeks of global data to obtain an accurate HNO_3 zonal mean diurnal variation for some mid-latitude altitudes. Systematic errors were not considered which could significantly affect these estimates of accuracy.

E. Journal Publications. No publication of the initial results has been made.

SUMMARY OF WORK PERFORMED ON PROJECT
ANALYSIS OF SAM II AEROSOL DATA

A) Full Title of Research Task

Analysis of SAM II Aerosol Data

B) Investigators and Institutions

Dr. Patrick Hamill
Systems and Applied Sciences Corporation
200 California Avenue, Suite 210
Palo Alto, CA 94306

(Dr. Hamill is also associated with:
Physics Department, San Jose State Univ.
San Jose, CA 95192)

C) Abstract of Research Objectives

The principal objective of this research project is to carry out an analysis of the data obtained by the NASA SAM II satellite system and to evaluate the general characterisics of the stratospheric aerosol layer and the occurrence of polar stratospheric clouds. Specifically, the work being performed focuses on the conditions when polar stratospheric clouds (PSC's) are formed, the microphysical mechanisms involved in PSC formation, and the sedimentation of cloud particles and/or the subsidence of the aerosol layer as a possible sink for stratospheric water vapor. A related research objective is to carry out statistical studies of the PSC observations obtained during the past five years to determine temporal and geographic trends in PSC occurrences. Finally, an overall general objective of the project is to utilize the SAM II data to obtain a more precise characterization of the properties of the stratospheric aerosol layer.

D) Summary of Progress and Results

Although work on this project has only recently commenced, a number of concrete results have been obtained.

The data set being analyzed consists of atmospheric extinction measurements made by the Stratospheric Aerosol Measurement experiment (SAM II) which is mounted on the NASA Nimbus 7 satellite. Due to the orbital parameters of this satellite, the measurements are taken at high latitudes. An analysis of the SAM II data revealed the surprising fact that stratospheric clouds are fairly common during the winter when temperatures in the polar stratosphere are below about -83° C. The analysis of the formation and occurrence of these clouds soon became a significant research item as scientists questioned whether or not the clouds could affect climate/radiation balance or the the stratospheric water vapor budget.

The importance attached to the study of the polar stratospheric clouds is underlined by the fact that a NASA workshop on "Polar Stratospheric Clouds: Thier Role in Atmospheric Processes" was held in June 1983 in Virginia Beach, VA. Patrick Hamill, the principal investigator of this project, served as chairman of the workshop and is presently editing a document summarizing the workshop deliberations. This docuement will probably be published as a NASA Conference Publication. The workshop was make possible by funding through the office of Dr. R. T. Watson. The participants of the workshop made a number of recommendations to NASA, including a continued analysis of the SAM II data, modeling studies of PSC's, and a number of experimental measurements.

The research project has as one of its principal objectives a year-by-year analysis of the SAM II data to determine the number of stratospheric clouds found in a given winter, the altitudes at which they appear, and the correlation of cloud formation with temperature. This work is well underway and preliminary results of the analysis were presented at the IUGG General Assembly in Hamburg, Germany in August, 1983 by Patrick Hamill. A journal article describing these results is in preparation.

Other work which is presently being carried out includes an analysis of the the sedimentation of cloud particles. A great deal of effort at present is being expended on preliminary work such as the preparation of computer programs to carry out the appropriate analyses of the SAM II data.

E) Journal Publications

None.

September 9, 1983

A. Title of Research Task

Correlative studies and analyses of recent satellite ozone data.

B. Investigators and Institutions

F. Luther, J. Lovill, J. Ellis
Lawrence Livermore National Laboratory
Livermore, California

C. Research Objectives

This research involves the analysis and interpretation of satellite ozone data with the goal of developing an increased understanding of physical processes in the upper atmosphere. The major emphasis is correlative studies among data from various satellite ozone sensors. Comparisons between data sets will be made involving millions of data point comparisons within specified ground separation distance limits and overpass time intervals.

D. Progress and Results

The funding for this project began in 1983 and initial studies have begun. The satellite data intercompared thus far are from the TOMS and SBUV sensors on Nimbus G, the TOVS sensor on TIROS-N and the MFR sensor on a DMSP satellite. Analyses to date have been for a short time period (one week) in July 1979. The TOMS and SBUV sensors were observed to measure less total ozone than the MFR sensor, the differences being 10 and 15 Dobson Units (DU), respectively. The MFR and TOMS sensors measured less ozone than the TOVS sensor, the differences being 19 and 28 DU, respectively. These differences were latitudinally dependent with greatest differences between sensors occurring at the higher latitudes in the Northern Hemisphere.

E. Journal Publications

Lovill, J. and J. Ellis, "Correlative studies of satellite ozone sensor measurements," Geophys. Res. Lett., 10, 447-450, 1983.

Research Summary

A. Task: Stratospheric Dynamics and Transport

B. Investigators: C. B. Leovy and D. L. Hartmann, Department of Atmospheric Sciences AK-40, University of Washington, Seattle, Washington 98195

C. Abstract of Research Objectives: This research is aimed at improving our understanding of the factors responsible for interannual variability in the stratosphere by detailed analysis of satellite and other data sets. Particularly intensive use is made of Nimbus 7 LIMS satellite data. Four focal points of the research are: the mechanisms of the semi-annual oscillation, the interaction between planetary waves of high latitude origin and the low latitude critical surface, the properties and causes of propagating planetary waves, mechanisms of ozone transport in the middle and upper stratosphere.

D. Summary of Progress and Results: Nimbus 7 LIMS data on temperature and ozone have been compared with data from other satellite and *in situ* sensors in an effort to determine the distribution of systematic LIMS errors and assess the unique information content of the LIMS data. Reliable gradient zonal winds can be constructed from LIMS data, and the structure of the equatorial semi-annual oscillation has been depicted in much greater detail than before. Fluctuating temperatures reveal the structure of equatorial Kelvin waves between 30 and 60 km and discrete wave packet propagation is shown to occur in the Oct.-Mar. period, while steady waves occur in Apr.-May. Packet dispersion, wave interactions with shear zones, and associated mean wind changes are shown to be in good agreement with equatorial wave theory. Temperature structures are also shown to give the first direct evidence for cross equatorial mixing by inertially unstable motions near the stratopause.

LIMS data are shown to provide valid information on ozone fluctuations in the difficult lower stratospheric region 30-100 mb. In the middle stratospheric region 3-30 mb, ozone variations are shown to be consistent with the recent McIntyre-Palmer model of planetary wave breaking. Details of the vertical structure and time evolution of wave breaking are revealed by ozone, and ozone variations in the winter polar cap during warming events are characterized.

E. Publications 1982-83:

Smith, A. K., 1983: Stationary waves in the winter stratosphere: seasonal and interannual variability. *J. Atmos. Sci.*, *40*, 245-261.

Leovy, C., M. Hitchman, A. Smith, J. Gille, P. Bailey, L. Lyjak, J. Russell, L. Gordley, E. Remsberg, M. Salby, 1983: Properties of quasi-global fields of temperature geopotential and wind derived from the Nimbus 7 LIMS experiment. *J. Geophys. Res.* (submitted).

TITLE OF RESEARCH TASK: Utilization of SAGE Aerosol Profiles in the Analysis of Mauna Loa Stratospheric Lidar Data

INVESTIGATORS: Frederick G. Fernald, Physics Department, University of Denver
David G. Murcray, Physics Department, University of Denver

RESEARCH OBJECTIVES:

SAGE stratospheric aerosol profiles will be used to improve the analysis and interpretation of stratospheric lidar observations collected at the Mauna Loa Observatory. In order to derive the absolute scattering properties of the particulate and molecular scatterers from stratospheric lidar observations, it is necessary to establish; (1) initial criteria for the instrument calibration, (2) values for the ratio of the extinction to backscattering cross-sections of the scatterers and their variations with height, and (3) in the case of the Mauna Loa lidar, the mean aerosol backscattering cross-section near the maximum range of the system at 30 km above sea level. The results of the lidar analyses are very dependent on these initial assumptions which, to date, have not been rigorously established. SAGE aerosol extinction profiles provide a means of establishing them and assessing the uncertainties associated with them.

SUMMARY OF PROGRESS AND RESULTS:

This report covers the period from July 1, 1983 to September 1, 1983. Work under this research project has just begun. Considerable headway has been made in the development of computer software required for the analysis of the SAGE and Mauna Loa data sets. Extensive error analyses have been added to the existing lidar analysis program. Work is progressing on the software used to transcribe and plot the SAGE data tapes. Once this phase has been completed, the actual comparisons of the SAGE and Mauna Loa data sets can begin.

Title: Analysis of Stratospheric Ozone and Minor Constituents

Principal Investigator: R. S. Stolarski
NASA/Goddard Space Flight Center
Code 964
Greenbelt, MD 20771

Co-Investigators: M. A. Geller
J. C. Alpert
M.-F. Wu
C. H. Jackman
NASA/Goddard Space Flight Center
Code 964
Greenbelt, MD 20771

The LIMS constituent data has been recently acquired from NSSDC. We are now experimenting with a variety of ways to determine best values for unmeasured constituents to be used to construct estimates of the net photochemical production of ozone as a function of altitude, latitude and season. Mapped SBUV ozone data has been obtained from NOAA and is being used together with dynamics information derived from temperature data to derive ozone fluxes. The convergences and divergences determined from these fluxes will be compared with the net photochemical production terms for consistency. These data are being used to construct an initial condition for a one to two week forecast run using the 3D stratospheric GCM. The period before and during the February 1979 major warming is being emphasized.

Analysis has begun to compare the SBUV ozone measurements during the February, 1979 major warming with temperature measurements from the SSU. At 1 mb temperature-ozone anticorrelations are quite evident but some intriguing breakdowns are being investigated further. In addition to providing initial conditions for the forecast run and measurements against which to compare results these studies are providing a test of the chemical parameterizations being developed for 3D ozone-dynamics feedback models.

Summary Report on

"A Statistical Analysis of Stratospheric Ozone Profile Data from the Nimbus-4 and Nimbus-7 Satellites"

by

Gregory C. Reinsel

Department of Statistics
University of Wisconsin-Madison

Abstract of Research Objectives

Our principal interest lies in the analysis of available profile ozone data from the Nimbus-4 BUV satellite experiment for the period April 1970 to April 1977 and from the Nimbus-7 SBUV satellite experiment for the period November 1978 to October 1980. We analyze monthly averages of satellite profile data in the upper five Umkehr layers, which cover an altitude range from about 24 to 48 km, to obtain trend estimates of ozone change over this period. We wish to study the variations in these trend estimates as a function of altitude and geographic location. We also seek to determine the extent to which these two separate satellite data sets can be linked together in a combined analysis of trends in profile ozone, and to determine the accuracy of the resulting trend estimates.

Summary of Progress and Results

In any trend analysis based on the combined set of Nimbus satellite ozone data, it is essential to identify any instrument bias or other inconsistencies that may exist between the two satellite data sets. Without detailed information on the inter-calibration of the two satellite instruments, it seems necessary to approach this problem by the use of the ground based Umkehr profile data as a link to compare with the Nimbus satellite data. However, we have become aware of the existence of errors in the Umkehr measurements caused by the presence of stratospheric aerosols, and these errors need to be accounted for when using the Umkehr data for the purpose of comparison with satellite data. Hence in our initial investigation, a statistical analysis of ozone profile data from the Umkehr method has been considered for the detection of trends, where possible effects of stratospheric aerosols on the Umkehr measurements have also been investigated and accounted for.

In this statistical trend analysis, time series models have been estimated using monthly averages of Umkehr data over the period 1958-1980 at each of 13 Umkehr stations, and at each of the five highest Umkehr layers 5-9. The time series regression models incorporate seasonal, trend, and noise factors, and an additional factor to explicitly account for the effects of atmospheric aerosols on the Umkehr measurements. For each Umkehr station, the explanatory series used in the statistical model to account for the aerosol effect is a constant multiplier times the five month running average of the monthly atmospheric transmission data at Mauna Loa, Hawaii, the only long running aerosol data available. The constant multiplier is estimated empirically for each individual station from the Umkehr data.

A random effects model is used to combine the individual station trend estimates from the time series models for each station, yielding the following 95% confidence interval estimates for overall ozone change over the period 1970-1980:

$$(-.29 \pm .39)\% \text{ per year for layer 9,}$$
$$(-.30 \pm .16)\% \text{ per year for layer 8,}$$
$$(-.22 \pm .17)\% \text{ per year for layer 7,}$$
$$(-.00 \pm .11)\% \text{ per year for layer 6,}$$
$$(-.04 \pm .14)\% \text{ per year for layer 5.}$$

Thus the results of this analysis suggest statistically significant decreases in ozone in Umkehr layers 7 and 8, which cover the 34 to 43 km altitude range, during the period 1970-1980, when the effects of atmospheric aerosols are incorporated in the statistical time series model. The estimated aerosol effect on the Umkehr data, that is, the effect of the atmospheric transmission variable in the time series model, was found to be largest in the uppermost two or three Umkehr layers(7-9), reasonably consistent with previous theoretical results concerning aerosol effects on Umkehr data. The empirically derived estimates of the aerosol effect are, on the average, equal to about 2.3, 3.7, and 5.7 percent change in Umkehr data per .01 change in transmission data for layers 7, 8, and 9, respectively.

Recently, we have begun the trend analysis of the combined set of Nimbus satellite data, comparing ozone levels of Nimbus-7 profile data for the two year period November 1978 to October 1980 with those of the corresponding Nimbus-4 data for the period April 1970 to November 1972 (a period for which instrumental drift in the Nimbus-4 data is thought to be minimal). To complete this analysis, comparisons of Nimbus data with ground-based Umkehr data, for which the empirical aerosol correction results are incorporated, will be required in order to attempt to estimate the extent to which any differences between the Nimbus-4 and Nimbus-7 data are due to instrumental and algorithmic differences as compared to actual changes in ozone amounts in the upper layers between 1970 and 1980.

Publications

Reinsel, G., G.C. Tiao, R. Lewis, and M. Bobkoski, Analysis of upper stratospheric ozone profile data from the ground-based Umkehr method and the Nimbus-4 BUV satellite experiment, Journal of Geophysical Research, 88, 5393-5402, 1983.

Reinsel, G., G.C. Tiao, J.J. DeLuisi, C.L. Mateer, A.J. Miller, and J.E. Frederick, Analysis of upper stratospheric Umkehr ozone profile data for trends and the effects of stratospheric aerosols, submitted for publication to the Journal of Geophysical Research, 1983.

A. Interpretation of Data from the Infrared Limb Scanners LRIR and LIMS

B. John C. Gille
National Center for Atmospheric Research

C. Research Objectives

The limb scanning experiments provided measurements of temperature, ozone, water vapor, nitric acid and nitrogen dioxide with high vertical resolution for this 7 month period. The objectives of this research are to evaluate these data, use them to solve problems of chemistry, dynamics and radiation in the stratosphere and mesosphere, and develop improved algorithms to interpret the data. Particular objectives include the presentation and explanation of the distribution and variation of the observed quantities. Problems to be studied include those of ozone, nitrogen and water vapor chemistry; sudden warmings, meridional circulation, energetics, and traveling waves; transports of trace constituents; and solar effects on the atmosphere. Additional problems can be addressed using LIMS data with SBUV, SAGE, and SAMS data.

D. Summary of Progress and Results, 1982-83

This summary also covers work under similar tasks which preceeded the present one.

The LIMS data were objectively analyzed early in 1982, in order to allow maps of the global distribution of temperature and trace gases, and to facilitate the calculation of winds and dynamical quantities. At the same time, the LRIR data were re-inverted, using inversion algorithms similar to those used for LIMS. It was necessary to modify the analysis algorithm for the LRIR summer period, because of less complete data coverage.

A considerable effort was put into the evaluation of the accuracy and precision of the LIMS data. This was done through numerical simulations, as well as studies of the internal consistency of the data and their comparison with other measurements. Near the conclusion of this process, a second LIMS retrieval was introduced. The same process was carried out for the new data. Subsequently, the experiment team decided to archive the second retrieval. The evaluation has been completed for the second data set, and the results submitted for publication. The LIMS data accuracy and precision were shown to be very good. They will find ready application to many problems of the upper atmosphere.

A large part of the initial effort has been a study of the disturbed winter of 1978-79. Zonal mean winds, heat and momentum transports, and Eliassen-Palm (EP) flux vectors were calculated for the entire winter. The westerly winds are strongest in December, but are slowed by interactions with planetary waves. These eventually bring about three warming events, including a major warming and reversed wind flow in late February. The EP flux convergence was found to be an excellent indicator in space and time of westerly wind deceleration. On the other hand, the refractive index gives the direction of planetary wave propagation only in an approximate sense. An initial descriptive paper is in press; a more detailed, quantitative evaluation of theoretical ideas is now being carried out.

Other studies show that wave-wave interactions are very important at times, and not just wave interactions with the mean westerlies. One paper is now in press, and another has been submitted for publication.

The winds have been used to calculate the transport of ozone, both in the traditional Eulerian way and by the quasi-Lagrangian residual mean circulation. The results are similar, but the residual mean results appear to lead to a more physical interpretation.

The time series of LIMS ozone data was used with the SBUV observations of solar UV irradiance to look for response to solar variations. After filtering the data and cross spectral analysis, a clear signal was seen, showing that the ratio of the percent change of ozone to the percent change of solar UV (at 205 nm) ranges from 0.2-0.5, in good agreement with model results. If the 205 nm radiance varies by 20% over an 11 year solar cycle, it implies a 10% ozone change from 32-46 km layer, similar to values suggested by Umkehr results. These results appear to be the clearest and most quantitative indication that solar variations cause changes in atmospheric ozone. These results have been submitted for publication. Several other studies are in early, exploratory phases.

E. Publications

Gille, J. C., P. L. Bailey, L. V. Lyjak, and J. M. Russell III, 1983: Results from the LIMS experiment for the PMP-1 Winter 1978/79. _Adv. Space. Res._, _2_, 163-167.

Gille, J. C. and L. V. Lyjak, 1983: An overview of wave-mean flow interactions during the winter of 1978-79 derived from LIMS observations. _Adv. Earth Plan. Sci._, in press.

Gille, J. C., C. M. Smythe, and D. F. Heath, 1983: Observed ozone response to variations in solar UV. Submitted to _Science_.

Drayson, S. R., P. L. Bailey, H. Fischer, J. C. Gille, A. Girard, L. L. Gordley, J. E. Harries, W. G. Planet, E. E. Remsberg, and J. M. Russell 111, 1983: Spectroscopy and transmittances for the LIMS experiment. Submitted to _J. Geophys. Res._

Gille, J. C., and J. M. Russell III, 1983: The Limb Infrared Monitor of the Stratosphere (LIMS): An overview of the experiment and its results. Submitted to _J. Geophys. Res._

Gille, J. C., J. M. Russell III, P. L. Bailey, L. L. Gordley, E. E. Remsberg, J. H. Lienesch, W. G. Planet, F. B. House, L. V. Lyjak, and S. A. Beck, 1983: Validation of temperature retrievals obtained by the Limb Infrared Monitor of the Stratosphere (LIMS) experiment on Nimbus 7. Submitted to J. Geophys. Res.

Gille, J. C., J. M. Russell III, P. L. Bailey, E. E. REmsberg, L. L. Gordley, W. F. J. Evans, H. Fischer, B. W. Gandrud, A. Girard, J. E. Harries, and S. A. Beck, 1983: Accuracy and precision of the nitric acid concentrations determined by the Limb Infrared Monitor of the Stratosphere (LIMS) experiment on Nimbus 7. Submitted to J. Geophys. Res.

Russell, J. M., III, J. C. Gille, E. E. Remsberg, L. L. Gordley, P. L. Bailey, H. Fischer, A. Girard, S. R. Drayson, W. F. J. Evans, and J. E. Harries, 1983: Validation of water vapor results measured by the Limb Infrared Monitor of the Stratosphere (LIMS) experiment on Nimbus 7. Submitted to J. Geophys. Res.

Russell, J. M., III, J. C. Gille, E. E. Remsberg, L. L. Gordley, P. L. Bailey, S. R. Drayson, H. Fischer, A. Girard, J. E. Harries, and W. F. J. Evans, 1983: Validation of nitrogen dioxide results measured by the Limb Infrared Monitor of the Stratosphere (LIMS) experiment on Nimbus 7. Accepted by J. Geophys. Res.

Remsberg, E. E., J. M. Russell III, J. C. Gille, L. L. Gordley, P. L. Bailey, W. Planet, and J. E. Harries, 1983: The validation of Nimbus 7 LIMS measurements of ozone. Submitted to J. Geophys. Res.

Leovy, C. B., M. H. Hitchman, A. K. Smith, J. C. Gille, P. L. Bailey, L. V. Lyjak, and E. E. Remsberg, 1983: Properties of quasi-global fields of temperature, geopotential and wind derived from the Nimbus 7 LIMS experiment. Submitted to J. Geophys. Res.

Smith, A. K., 1983: Observations of wave-wave interactions in the stratosphere. J. Atmos. Sci., October issue.

Smith, A. K., Gille, J. C., and L. V. Lyjak, 1983: Wave-wave interactions in the stratosphere: Observations during quiet and active wintertime periods. Submitted to J. Atmos. Sci.

B. INTERPRETATION OF AIRCRAFT AND BALLOON DATA

Title of Research Task: Water Vapor Removal and Its Relationship to Stratosphere-Troposphere Exchange in the Tropics as Revealed by the 1980 NASA ITCZ Panama Experiments

Investigators and Institutions: L. Pfister, R.A. Craig, and W.L. Starr -- all of NASA Ames Research Center, Moffett Field, CA

Research Objectives:

The aim of this work is to gain an understanding of the role of cumulus towers and cumulus cloud clusters in the transport of trace species from the troposphere to the stratosphere in the tropics. Three types of data, all from two days during the September 1980 NASA Panama water vapor exchange experiment, will be utilized to develop a coherent picture of the distribution of various chemical and meteorological quantities in the neighborhood of cumulus cloud tops: U-2 aircraft data taken at 5 second (or shorter) intervals, particularly particle counts, total water, ozone, temperature, and pressure; radiosonde-ozonesond data every 12 hours; and IR satellite images every 30 minutes. The approach is to use the radiosonde data to establish average vertical profiles of the meteorological variables in the region, the satellite images, aircraft position data, and particle counts to show cloud structure where the aircraft flew, and the aircraft chemical and meteorological data for structures in the neighborhood of the clouds. We are particularly interested in evidence that chemical species have been moved across potential temperature surfaces, either by mixing driven by cumulus clouds or radiative diabatic cooling due to the cold cumulus cloud tops.

Progress and Results:

Data reduction for the flights on the two days of interest (i.e., interpolation of the various datasets to the same time scale; elimination of bad data) has been completed. Up to this point, however, we have focussed our attention on a large, isolated anvil fromed during the September 12 flight which was penetrated and overflown several times by the aircraft. Our results pertain mostly to this one case.

At the level of the anvil (about 16.9 km), overall ozone is depressed relative to the flight-averaged value for that altitude, consistent with what is expected when ozone-poor tropospheric air is mixed into the lower stratosphere. The ozone distribution at this level is by no means uniform, however. In fact, ozone values are anomalously high when the aircraft passes through the thickest part of the anvil, as defined by the total water content of the air. The potential temperature is also anomalously high in these regions. This shows that cumulus turrets not only penetrate well into the stratosphere, but that they mix with the air at those levels before sinking down to the equilibrium (anvil) level.

When the aircraft overflew the turret and anvil region at about 18.5 km, substantial horizontal gradients of ozone and potential temperature were observed, with low values of these variables over the central part of the anvil, and high values over the clear regions and the edge of the cloud shield. Present indications are that most of these gradients can be explained by a quasi-conservative uplift associated with the mass inflow of of tropospheric air caused by the cumulus convection. However, there is some indication that the ozone values are lower than would be indicated by this process, suggesting either diabatic heating, or a mixing process which alters the ozone-potential temperature relationship. We are presently evaluating the statistical significance of the change in the ozone-potential temperature relationship. We have found no evidence of ozone enhancement above a cloud shield associated with sinking due to diabatic cooling.

Publications: None to this date.

A. Title of Task

"Study of Stratosphere-Troposphere Mass Exchange"

B. Investigators and Institution

G.D. Robinson (Principal Investigator), and M.G. Atticks
The Center for the Environment and Man, Inc., Hartford, CT

C. Abstract of Research Objectives

The research is concerned with the mechanism by which tropospheric air reaches the photochemically active regions of the stratosphere. The working hypothesis is that this transfer occurs only in the equatorial zone between about 10°N and 10°S, any transfer in other latitudes being locally reversible and affecting only the lowest chemically inactive layer of the stratosphere. Water is removed from the transferred air by condensation and precipitation, very low temperatures ($< -80^{\circ}C$) being required to produce the observed water content. There are unresolved difficulties of detail in explaining the process. The research objective is to clarify this detail. The practical importance relates to the development of realistic models of the entry of tropospheric pollutants into the photochemically active regions of the stratosphere. If the hypothesis is correct, reactive or soluble pollutants emitted in temperate latitudes should be to a considerable extent removed in the transfer process.

D. Summary of Progress and Results

The method adopted involves study of the detailed temperature structure near the tropical tropopause in a large number of individual radiosonde ascents, in conjunction with satellite imagery of clouds and satellite measurements of the infrared radiance (temperature) of cloud tops. The observed structures are compared with those expected to be associated with variants of the cooling and precipitation process.

Statistics of the occurrence of very low temperatures have been constructed for one year (1979, during the FGGE). These establish that conditions suitable for production of stratospheric air occur most frequently in the eastern hemisphere and northern winter, but are not entirely absent in some longitude zones in the northern summer. Soundings with temperature structures allowing production of stratospheric type air occur in both cloudy and cloud-free areas. Temperature structures expected to be associated with certain proposed mechanisms of the precipitation process have not yet been observed, but it is clear that there is complex dynamical activity on a wide range of spatial scales in a tropopause zone several kilometers thick. Any numerical models directed at the problem of anthropogenic effects on stratospheric chemistry must be compatible with these observations.

E. Publication

M.G. Atticks and G.D. Robinson, "Some Features of the Structure of the Tropical Tropopause," Quart. J. Roy. Meteor. Soc., Vol. 109, pp. 295-308, 1983.

Studies of the Global Budget of Stratospheric Water Vapor

Principal Investigator: Dr. John E. Frederick
Code 964
NASA/Goddard Space Flight Center
Greenbelt, MD 20771

Research Objectives:

The objectives of this task are to increase our understanding of the spatial and temporal variability of water vapor in the stratosphere by examining a time series of temperature measurements taken in the vicinity of the tropical tropopause. Major items of concern include (1) testing the consistency between observed water vapor abundances in the lower stratosphere and the saturation mixing ratio appropriate to the tropical tropopause and (2) examining the daily and seasonal cycle in observed temperatures as a potential indicator of both the expected variability in stratospheric water vapor and temporal variations in the strength of troposphere to stratosphere transport.

Summary of Progress and Results:

An analysis of temperature measurements obtained over an 8 year period in the vicinity of the low latitude tropopause has confirmed the existence of longitude regions which are consistently colder by roughly 2-3 K than elsewhere in the tropics. Study of the vertical profiles shows, however, that these temperature differences are confined to a layer of thickness 3-5 km centered on the tropopause. The lowest monthly mean temperatures observed at the colder stations during the annual cycle yield saturation mixing ratios that are consistent with the range of measured stratospheric water vapor. Examination of the daily variations in temperature at a given station reveals a more complex pattern than indicated by the monthly averages. On many days temperatures at the colder longitudes corresponds to water vapor abundances that are substantially less than observed in the stratosphere despite the favorable comparison of the monthly means. The results point to the need for a series of water vapor soundings at selected longitudes and times in order to define the extent to which the tropical tropopause temperature influences the stratospheric water vapor abundance.

Journal Publications:

Frederick, J. E., and A. R. Douglass, Atmospheric temperatures near the tropical tropopause: Temporal variations, zonal asymmetry, and implications for stratospheric water vapor, Mon. Wea. Rev., in press, to appear in July 1983 issue.

A Critical Examination of Upper Stratospheric Measurements and the Odd Oxygen Photochemical Balance

Principal Investigator: Dr. John E. Frederick
Code 964
NASA/Goddard Space Flight Center
Greenbelt, MD 20771

Research Objectives:

This task consists of two primary efforts. The first involves examining the behavior of backscattered radiances obtained by the backscatter ultraviolet radiometers on the Nimbus 4 and 7 satellites over long periods of operation. The purpose here is to seek long term trends of both instrumental and geophysical origin and to develop methods for distinguishing these two sources of variation in a radiance data base. The second aspect involves using ozone profile measurements obtained by satellites in conjunction with photochemical model calculations to seek the origin of discrepancies that exist between measurement and theory, particularly in the upper stratosphere. In conjunction with this effort studies of the penetration of ultraviolet radiation into the middle atmosphere are being conducted as well as geophysical interpretation of trace gas measurements obtained by rockets in the upper stratosphere and mesosphere.

Summary of Progress and Results:

Analysis of the 7 year backscattered ultraviolet data base from Nimbus 4 reveals a long term increase in the radiances that is a function of wavelength, with the greatest changes occurring at the short end of the spectrum. Taken alone this could be indicative of the changing sensitivity of the instrument. However, the drift displays a very clear latitude dependence with the greatest radiance increases occurring in the Southern Hemisphere. For example, the backscattered wavelength 273.5 nm, which senses ozone in the 45-55 km region, shows an increase of 1.2% per year in the latitude band 30-45°N, while the corresponding value for 30-45°S is 2.1% per year. It is difficult to reconcile this behavior with an instrumental change alone. The data suggest a true change in upper stratospheric ozone between 1970 and 1977 with the most pronounced effect in the Southern Hemisphere. The fact that the data represent a convolution of changes in instrument sensitivity and true geophysical effects greatly complicates the interpretation and additional work must be done in this area. Comparison of the radiance drifts with those expected theoretically on the basis of a CFM-related depletion shows no similarity between the observed and predicted wavelength dependencies and magnitudes. However, the predicted CFM effects are sufficiently small that the observed radiance changes would overwhelm them, if indeed they are present.

Summary of Progress and Results (con't)

Additional efforts involved a new calculation of the atmospheric predissociation rate of nitric oxide which reveals that the opacity provided by thermospheric NO is a significant factor in determining the mesospheric and upper stratospheric results. In a separate study conducted with the University of Michigan, analysis of nitric oxide data obtained by a rocket-borne sensor showed a large variability near the stratopause indicating the important influence of transport processes on the distribution.

Journal Publications:

Frederick, J. E., F. T. Huang, A. R. Douglass, and C. A. Reber, The distribution and annual cycle of ozone in the upper stratosphere, J. Geophys. Res., 88, 3819, 1983.

Frederick, J. E., R. B. Abrams, and P. J. Crutzen, The delta band dissociation of nitric oxide: A potential mechanism for coupling thermospheric variations to the mesosphere and stratosphere, J. Geophys. Res., 88, 3829, 1983.

Horvath, J. J., J. E. Frederick, N. Orsini, and A. R. Douglass, Nitric oxide in the upper stratosphere: Measurements and geophysical interpretation, J. Geophys. Res., in press, 1983.

C. INTERPRETATION OF SPECTRAL DATA

Studies of the UV Spectroscopic Properties of the Stratosphere

Principal Investigators: Dr. Richard D. McPeters
Dr. John E. Frederick
Code 964
NASA/Goddard Space Flight Center
Greenbelt, MD 20771

Research Objectives:

The goals of this research task are twofold: first, to better understand the spectroscopic properties of the atmosphere in the middle ultraviolet by analyzing spectral data from the solar backscattered ultraviolet instrument (SBUV) on Nimbus 7, and second, to determine the distribution of nitric oxide with latitude and season using the intensities of NO fluorescence features in these spectra. Although the optical properties of the stratosphere are generally well understood, we find that when we attempt very high accuracy in our ozone retrievals (1 percent), uncertainties in the absorption coefficients and second order effects such as Raman scattering and resonance fluorescence features limit our accuracy. Radiance data in the wavelength range 200 nm - 400 nm are used to test the accuracy with which we can explain various effects. The relative intensities of the NO gamma band fluorescence features in these spectra give information on the total amount of NO above 45 km and the results are being used to study the NO climatology.

Summary of Progress and Results:

SBUV was operated in the continuous spectral scan mode for nine individual days in 1979 and preliminary data from these days have been analyzed to demonstrate that information on spectroscopic properties can be derived. We remove the orders-of-magnitude variation of the backscattered albedo by subtracting a theoretical spectrum calculated using only Rayleigh scattering and ozone absorption. The resulting difference plot clearly reveals inconsistencies in the 1 to 10 percent range between measurement and calculation.

Initial results showed anomalous features between 300 nm and 310 nm that proved to be the result of small errors in the published Inn and Tanaka ozone absorption coefficients. The features disappeared when the new Bass absorption coefficients were used.

Below 240 nm an increasingly large negative difference results from not including absorption by oxygen. But when we calculate the effective absorption coefficient for O_2, our results are almost 30 percent lower than the laboratory measurements. Our results confirm those of Frederick and Mentall which also require substantially lower O_2 absorption coefficients.

Summary of Progress and Results (con't)

Strong emission features are observed between 215 nm and 280 nm at exactly the wavelengths of the gamma band series of nitric oxide resonance fluorescence. The intensities of these bands have been used to calculate total NO above 45 km for 1 day, September 10, 1979. We find between 6.5 and 7.5 ($x10^{19}$) molecules per square centimeter in zones between 60°S and 75°N, but only 3.5 in the 75°S zone.

A calibrated continuous scan tape is now being prepared that will cover 4 years of operation. This will be used to extend and refine our present results.

Journal Publications:

Frederick, J. E., and R. B. Abrams, "Model studies of nitric oxide fluorescence in the Earth's backscattered spectrum," Planet. Space Sci., 30, 137-145, 1982.

McPeters, R. D., and A. M. Bass, "Anomalous atmospheric spectral features between 300 nm and 310 nm interpreted in light of new ozone absorption coefficient measurements," Geophys. Res. Lett., 9, 227-230, 1982.

Frederick, J. E., and R. B. Abrams, "Dayglow emissions of the O_2 Herzberg bands and the Rayleigh backscattered spectrum of the Earth," Planet. Space Sci., 30, 575-580, 1982.

McPeters, R. D., "The use of backscattered UV spectral scans to infer the global NO distribution," Topical Meeting on Optical Techniques for Remote Probing of the Atmosphere, mc24-1 - mc24-4, Optical Society of America, 1916, Jefferson Place, NW, Washington, DC 20036, January 10-12, 1983.

Title:

Analysis of IR Balloon Data for Trace Species

Investigators and Institutions:

R. K. Seals, Jr. (Langley Research Center)

Co-Investigators:

C. P. Rinsland (LaRC)
J. H. Park (LaRC)
M. A. H. Smith (LaRC)
A. Goldman (Univ. of Denver)
D. G. Murcray (Univ. of Denver)
R. E. Boughner (LaRC)
J. C. Larsen (Systems and Applied Sciences Corp.)

Abstract of Research Objectives:

The principal objective of this research is the comprehensive analysis and interpretation of infrared atmospheric spectra with emphasis on high resolution interferometric spectra from balloon platforms. The focus is on improvement/refinement of analytical techniques for retrieval of species, pressure, and temperature profiles and on application of these techniques to obtain quantitative data on stratospheric parameters. This research is pursued in collaboration with the University of Denver atmospheric spectroscopy program and with various experimenters involved in the stratospheric Balloon Intercomparison Campaigns (B.I.C.).

Summary of Progress and Results:

Research during 1982-1983 has been primarily in three areas: analysis of interferometric infrared absorption spectra of the atmosphere, development of techniques for modeling interferogram distortions, and initiation of independent analysis of spectra from the B.I.C. balloon flights. In collaboration with the University of Denver, a variety of studies utilizing spectra from balloon flights of their high resolution (0.02 cm^{-1}) interferometer in October 1978 (7.5 to 13μm) and in March 1981 (5 to 8μm) have been performed. New results on O_2 continuum absorption near 6.4μm, important in analysis of stratospheric remote sensor data, have been published. New laboratory data were coupled with the 1979 atmospheric spectra to retrieve the stratospheric profile of N_2O using Q-branch features near 5.3μm. The 1978 spectra have been analyzed using nonlinear least squares spectral curve fitting to derive the stratospheric temperature profile from 10.4μm CO_2 features. The study demonstrates the utility of this spectral band for providing temperature profile data as part of a comprehensive analysis of spectra covering this region. An iterative retrieval-photochemical model calculation technique which incorporates diurnal effects has been developed and applied to derivation of a sunset NO profile from the 1979 absorption spectra. These spectra have also been analyzed to derive simultaneous profiles of HDO, H_2O, and CH_4 which provide insight into the mechanisms controlling stratospheric H_2O. In addition to the balloon spectra studies, analysis has been done on ground-based absorption spectra recorded with the 0.01 cm^{-1} resolution interferometer at Kitt Peak National Observatory. One result has been new information on atmospheric concentrations of HCN.

In the area of modeling interferogram distortions, two major studies have been published. First, a method accounting for the "smearing" effect encountered in recording interferograms through the changing air mass of an occultation event was developed and applied to pressure and temperature retrievals from 4.3μm spectra. In addition, a Fourier transform technique for simulating interferogram distortions due to both intensity and phase errors was developed and applied successfully to both laboratory and atmospheric spectra.

Finally, work has begun on independent analysis of B.I.C. spectra. The first emphasis has been on adapting the Emissivity-Growth-Approximation, or EGA, technique developed for the LIMS satellite experiment to analysis of emission spectra obtained by the NPL spectrometer. Initial results for HNO_3 profile have been obtained from 11μm spectra.

JOURNAL PUBLICATIONS

Rinsland, C. P., M. A. H. Smith, R. K. Seals, Jr., A. Goldman, F. J. Murcray, D. G. Murcray, J. C. Larsen, and P. L. Rarig: Stratospheric Measurements of Collision-Induced Absorption by Molecular Oxygen. J.G.R., 87, April 1982.

Park, J. H.: Effect of Interferogram Smearing on Atmospheric Limb Sounding by Fourier Transform Spectroscopy. App. Optics, 21, April 1982

Rinsland, C. P., A Goldman, F. J. Murcray, D. G. Murcray, M. A. H. Smith, R. K. Seals, Jr., J. C. Larsen, and P. L. Rinsland: Stratospheric N_2O Mixing Ratio Profile from High-Resolution Balloon-Borne Solar Absorption Spectra and Laboratory Spectra Near 1880 cm^{-1}. App. Optics, 21, Dec. 1982

Rinsland, C. P., M. A. H. Smith, P. L. Rinsland, A. Goldman, J. W. Brault, and G. M Stokes: Ground-Based Infrared Spectroscopic Measurements of Atmospheric Hydrogen Cyanide. J.G.R. 87, Dec. 1982.

Park, J. H.: Analysis Method for Fourier Transform Spectroscopy. App. Optics, 22, March 1983.

Smith, M. A. H., and L. L. Gordley: Sensitivity of Ozone Retrievals in Limb-Viewing Experiments to Errors in Line-Width Parameters, J.Q.S.R.T., 29, 1983.

Rinsland, C. P., A. Goldman, F. J. Murcray, D. G. Murcray, M. A. H. Smith, R. K. Seals, Jr., J. C. Larsen, and P. L. Rinsland: Stratospheric Temperature Profile from Balloon-Borne Measurements of the 10.4μm Band of CO_2. J.Q.S.R.T., in press, 1983.

Rinsland, C. P., D. C. Benner, D. J. Richardson and R. A. Toth: Absolute Intensity Measurements of the $(11^10)_{II} \leftarrow 00^00$ Band of $^{12}C^{16}O_2$ at 5.2μm. App. Optics, accepted for publication 1983.

Title: Measurement of Stratospheric Light Nonmethane Hydrocarbons and Peroxyacetyl Nitrate by Analysis of Air Samples

Investigators: Principal Investigator: A. C. Aikin
Co-Investigators: E. J. Maier
J. R. Herman
Goddard Space Flight Center
Greenbelt, MD 20771

C. W. Spicer
Battelle Laboratories
Columbus, OH 43201

Abstract:

The low chemical reactivity of the simplest nonmethane hydrocarbons such as ethane, allows them to penetrate into the stratosphere before they are destroyed photochemically. One of the products of this destruction is peroxyacetyl nitrate which can occur in sufficient concentrations in the lower stratosphere to be an important reservoir for odd nitrogen. In order to test this theory it is necessary to measure the altitude distribution of the nonmethane hydrocarbons and PAN. Whole air samples taken at different altitudes in the lower stratosphere by the techniques of cryosampling and evacuated spheres are analyzed by gas chromatography. Resulting measurements are compared with models. In addition models are being developed which extend the hydrocarbon chemistry and transport. Available atmospheric infrared absorption and emission spectra will be analyzed for hydrocarbons, PAN and other products.

Progress and Results:

A cooperative effort has been formed to use balloon-borne sampling apparatus available and under the direction of C. Gallagher of the Air Force Geophysical Laboratory. Available systems include a three chambered liquid helium cryosampler to allow sampling at three altitudes as well as evacuated

Title: Measurement of Stratospheric Light Nonmethane Hydrocarbons and Peroxyacetyl Nitrate by Analysis of Air Samples
Principal Investigator: A. C. Aikin

Progress and Results (con't)

spheres. Under the direction of C. Spicer, Battelle Laboratories performs calibration of the sampling system and analysis of returned samples. The systems have been calibrated for hydrocarbons and both cryosampling and evacuated spheres have been shown to retain the samples. The calibration for peroxyacetyl nitrate is currently in progress and a fall 1983 balloon launch is planned.

Calculations have shown that peroxyacetyl nitrate arises mainly from the destruction of ethane in the 10 to 25 km altitude range. The concentration is very sensitive to thermal decomposition and the molecule has a long lifetime at the tropopause and in the lower stratosphere. The concentration will depend on latitude and season with the longest lifetime occurring at high latitudes in winter. PAN may be as important as nitric acid for the storage of odd nitrogen in the lower stratosphere.

Publications:

Aikin, A. C., J. R. Herman, E. J. Maier and C. J. McQuillan, Atmospheric chemistry of ethane and ethylene, J. Geophys. Res., 87, 3105-3118, 1982.

Aikin, A. C., J. R. Herman, E. J. Maier and C. J. McQuillan, Influence of peroxyacetyl nitrate (PAN) on odd nitrogen in the troposphere and lower stratosphere. Accepted for publication Planetary and Space Sciences 1983.

V. ASSESSMENTS AND COORDINATION

DATA SURVEY AND EVALUATION

W. B. DeMore
Jet Propulsion Laboratory
Pasadena, CA 91109

Objectives

The purpose of this Task is to maintain an updated set of evaluated rate constants and photochemical cross sections for use in atmospheric modeling, and to publish the evaluated data in a form accessible to the community of atmospheric scientists.

Summary of Progress and Results

A series of five evaluations have been published, the most recent issue being in July of 1982. In March, 1983, a meeting of the evaluation panel was held for the purpose of preparing the sixth edition, which is currently in press.

Publications

1. "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling," Evaluation Number 5, JPL Publication 82-57, July, 1982.
2. "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling," Evaluation Number 6, in press, 1983.

Summary Report for the Contract
"Support of Middle Atmosphere Program Management"
NASW 3646

A. Title: Support of Middle Atmosphere Program Management

B. Investigators and Institution: C. H. Liu and S. A. Bowhill
Department of Electrical Engineering
University of Illinois at
Urbana-Champaign (UIUC)

C. Research Objectives:

This contract supports in part the activities associated with managing the International Middle Atmosphere Program (MAP) which started its intensive observational period on January 1, 1982. The major objective of MAP is to organize the coordinated global study of the composition, chemistry, structure, energetics, and motions of the middle atmosphere, from the tropopause to the mesopause. Fourteen MAP projects have been organized to carry out research activities in the effort to achieve this goal.

D. Summary of Progress and Results:

1. MAP Steering Committee Meetings:

Two MAP Steering Committee Meetings were held, one in Ottawa, Canada on May 17-19, 1982 and one in Hamburg, Germany, on August 13-14, 1983. During the meetings, reports from MAP Projects, MAP Study Groups and National MAP Representatives were presented. New MAP projects were proposed and approved. The future of MAP beyond the period of 1982-1985 was discussed. A Middle Atmosphere Cooperation (MAC) project for the period 1986-1988 was proposed to the SCOSTEP Bureau and received its approval.

2. MAP Projects:

Fourteen MAP projects are currently actively engaged in carrying out the different research goals of MAP. They are:

AMA - Antarctic Middle Atmosphere Program
ATMAP - Atmospheric Tides Middle Atmosphere Program
CAMP - Cold Arctic Mesopause Project
CLIMAT - Climatology of the Middle Atmosphere
DYNAMICS - Dynamics of the Middle Atmosphere in Winter-Coordinated Studies
GLOBMET - Global Meteor Observation System
GLOBUS - Global Budget of Stratospheric Trace Constitutents
GOSSA - Global Observations and Studies of Stratospheric Aerosols
GRATMAP - Gravity Waves and Turbulence in the Middle Atmosphere Program
MAE - Middle Atmosphere Electrodynamics
MSTRAC - MST Radar Coordination
OZMAP - Observations of and Sources of the Spatial and Temporal Variability of Ozone in the Middle Atmosphere on Climatological Time Scales
SSIM - Solar Spectral Irradiance Measurements
WINE - Winter in Northern Europe Project

3. MAP Study Groups:

Five new MAP Study Groups were organized to examine possible new areas for MAP projects. They are:

MSG-5 Ions and Aerosols
MSG-6 Scientific Aspects of an International Equaotiral Observatory
MSG-7 Penetration of Solar Radiation into the Atmosphere
MSG-8 Atmospheric Chemistry
MSG-9 Measurement of Middle Atmosphere Parameters by Long Duration Balloon Flights

4. MAP Workshops:

Five Workshops were held:

(i) Workshop on Comparison of Data and Derived Dynamical Quantities during Northern Hemisphere Winters, May 11-14, 1982, Boulder, CO
(ii) Workshop on Equatorial Middle Atmosphere Measurements and Middle Atmosphere radars, May 10-12, 1982, Boulder, CO
(iii) Workshop on Solar Spectral Irradiance Measurements, May 12-14, 1982, Washington, D. C.
(iv) PMP-1 Workshop, April, 1983, Oxford, UK
(v) Workshop on Technical Aspects of MST Radar, May 23-27, 1983, Urbana, IL

5. Data Management:

As observational results of MAP start to accumulate, plans have been drawn to facilitate data exchange and management. Surveys have been sent out to MAP scientists for the purpose of devising the most useful format and procedure for data management.

E. MAP Publications:

During this period, four volumes of HANDBOOK FOR MAP have been published (Vol. 4 through Vol. 7), and two are in the process of being published (Vol. 8 and Vol. 9).

SUMMARY OF 1982-83 RESEARCH

A. XV Informal Conference on Photochemistry

B. T. G. Slanger and D. M. Golden, SRI International

C. Partial support, joined by NSF, ARO, and ONR of the above symposium

D. The meeting took place at Stanford on June 27-July 1, 1982. Many papers were presented on all phases of photochemistry, including atmospheric processes, unimolecular reactions, bimolecular reactions, energy transfer, condensed phase systems, photophysics, and spectroscopy. It was considered to be a highly successful symposium.

E. A book of abstracts has been sent to the NASA office.

ORI, Inc.
1400 Spring Street
Silver Spring, Maryland 20910

Telephone (301) 588-6180

A. UPPER ATMOSPHERIC PROGRAMS BULLETIN

B. Florence M. Ormond, Editor
ORI, Inc.

C. The Upper Atmospheric Programs Bulletin is funded jointly by the National Aeronautics and Space Administration and the Federal Aviation Administration to facilitate and encourage communication among the scientific and technical communities interested in stratospheric research.

D. The Bulletin is distributed to approximately 3,500 scientists, engineers, and other technocrats throughout the world. Close coordination is maintained with NASA and FAA program managers and others engaged in stratospheric research in government, international organizations, private industry and academia. Contributions are received on a regular basis from principal investigators, authors and others interested in sharing information with colleagues. Contacts are also made directly with project managers or conference chairmen to obtain information on current activities or proposed investigations.

The Bulletin routinely reports on several categories. "News Highlights" focuses on major current activities. "Contributed Papers" is a section set aside to present abstracts of papers accepted for publication in the technical journals. "Recent Reports" presents news of published books or studies and informs readers on how to obtain copies of these reports. The "Forthcoming Events" section lists major open meetings and gives a brief rundown of pertinent data.

Significant articles which appeared in the Bulletin during 1982 and 1983 include:

- Photo-enhanced story on the International Intercomparison of Stratospheric Water Vapor Instrumentation.
- Report on a laboratory measurements program still in progress on Ultraviolet Absorption Cross Sections of O_3: The Temperature Dependence.
- Summary of Stratospheric Ozone Reports issued by U.S. Government agencies in response to the Clean Air Act Amendments of 1977.
- Recommendations of the FAA's High Altitude Pollution Program Scientific Advisory Committee presented during final meeting.

- Progress report on the International Intercomparison of Stratospheric Water Vapor Instrumentation.
- Recommendations of the NASA Panel for Data Evaluation for chemical rate constants and photochemical cross sections. Five tables of greatest general interest were reprinted for readers.
- Report on Global Habitability concept presented at the UNISPACE 82 Conference in August 1982 and news about Woods Hole Conference on global change and its impacts on habitability.
- New chlorofluorocarbons calculations made available from the Chemical Manufacturers Association.
- SSU Analyses - British Meteorological Office makes data available.
- Nimbus-7 SBUV/TOMS Ozone Results.
- Conferences, Meetings and Symposia regularly highlighted with program information, key participants, and details presented to feature these special meetings considered of interest.
- Photo-featured article on the first phase of the seven nation Balloon Intercomparison Campaign (BIC) conducted at the National Scientific Balloon Facility in Palestine, Texas.
- New Spectroscopic Line Parameters.
- Several Special Issues were published on Middle Atmosphere Programs.
- News and photos featuring the Reel Down experiment conducted by Harvard University.
- Lidar Observations of El Chichon seen in West Germany.
- Simultaneous In-situ Measurements of Stratospheric NO and NO_2.
- WMO Report on the climatic effects of ozone and trace gases.
- Balloon Ozone Intercomparison Campaign (BOIC) photo report.
- Executive Summary of UNEP meetings concerning atmospheric ozone.
- Global Tropospheric Experiment - long range research project.

UNITED STATES DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

September 2, 1983

Dr. Robert T. Watson
Code EE-8
NASA Headquarters
Washington, DC 20546

Dear Dr. Watson:

This letter is in response to your letter of August 10, 1983 requesting a summary of the research efforts supported by your office. The information is furnished in the format specified in your letter:

A. Chemical Kinetics Data Evaluation Activities in Support of the NASA Upper Atmospheric Research Program.

B. R. F. Hampson
Chemical Kinetics Division
National Bureau of Standards
Washington, DC 20234

C. The objective is to provide the reliable, evaluated reaction rate data base required as input data for the large scale modeling activities which form the basis for our understanding of the complex interactive chemistry of the atmosphere and which allow quantitative assessment of the effects of perturbation by man's activities.

D. The principal investigator has participated actively in the data evaluation activities of the NASA Panel for Data Evaluation on which panel he has the primary responsibility to review and evaluate the rate data for reactions of halogen-containing species. For these reactions updated and reevaluated data bases were presented at meetings of this panel held in January and March 1982 and in March 1983.

The principal investigator has also participated actively in the data evaluation activities of the CODATA Task Group on Chemical Kinetics with the primary responsibility to review and evaluate the rate data for the pertinent reactions of halogen and cyano radical species. For these reactions updated and expanded evaluated data bases were presented at Task Group meetings held in May 1982 and May 1983.

E. Baulch, D. L., Cox, R. A., Crutzen, P. J., Hampson, R. F., Kerr, J. A., Troe, J., and Watson, R. T., "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement I, "CODATA Task Group on Chemical Kinetics", J. Phys. Chem. Ref. Data, 11, 327-496 (1982).

DeMore, W. B., Watson, R. T., Golden, D. M., Hampson, R. F., Kurylo, M. J., Howard, C. J., Molina, M. J. and Ravishankara, A. R., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling: Evaluation Number 5", JPL Publication 82-57 (1982).

DeMore, W. B., Watson, R. T., Golden, D. M., Hampson, R. F., Kurylo, M. J., Howard, C. J., Molina, M. J. and Ravishankara, A. R., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling: Evaluation Number 6", JPL Publication 83-xx (1983).

Sincerely yours,

R. F. Hampson, Jr.

Robert F. Hampson
Chemical Kinetics Division
Center for Chemical Physics

UARP RESEARCH SUMMARY

A. Title of Research Task: Polar Stratospheric Clouds-Workshop on their Role in Atmospheric Processes

B. Investigators and Institutions:

Patrick Hamill	Chairman San Jose' State University Washington Square San Jose, CA 95192
Leonard R. McMaster	Co-Chairman NASA Headquarters, EE-8 Earth Science and Applications Division Washington, DC 20546

C. Abstract of Research Objectives:

The NASA Sam II sun photometer flown on the Nimbus 7 satellite has observed significantly enhanced extinction in both the Arctic and Antarctic polar stratosphere during local winter since it was launched in 1978. A preliminary investigation of these so-called polar stratospheric clouds and possible formation mechanisms revealed a high correlation between their occurence and temperature and led to the suggestion that their existence could have an impact on global water vapor and radiative budgets as well as polar climatology.[1] The objective of this task was to conduct a workshop to assess the current state of knowledge concerning polar stratospheric clouds, to assess their potential role in atmospheric processes, and to identify specific scientific problems worthy of future study which could be addressed by NASA.

[1] McCormick, M. P., H. M. Steele, P. Hamill, W. P. Chu, and T. J. Swissler: Polar Stratospheric Cloud Sightings by Sam II, J. Atm. Sci., 39, 6, 1387-1397 (1982).

II. Summary of Progress and Results:

A workshop entitled "Polar Stratospheric Clouds: Their Role in Atmospheric Processes" was held June 19-22, 1983, in Virginia Beach, Virginia. Approximately 20 scientists from universities and government laboratories reviewed the data collected by SAM II and other instruments on the observations of polar stratospheric clouds (PSC's) and reported on some preliminary modeling studies to ascertain the potential role of PSC's on climate, radiation balance, water vapor budget and other atmospheric processes. The participants are currently reviewing a draft report from this workshop which will be published as a NASA conference publication when completed.

Although the assessment of the role PSC's play in atmospheric processes has not been completed, the participants generally felt that the continued study of PSC's is justified as an interesting scientific problem which could be addressed by studies using common, well-established techniques even if their net effect on global radiation or water vapor budget was slight. The result of such studies would have a high probability of success since the PSC's present a simple system with few of the complicating factors which plague tropospheric studies. The results of such a study could expand our knowledge of microphysical processes, of hetereogeneous interactions in the stratosphere, and of the stratospheric water vapor budget. The results might help in understanding polar night chemistry and could perhaps serve as a test of some theories of the effect of clouds on the radiation balance and dynamics of the stratosphere. Finally the results of such studies could have the practical benefit of allowing a determination of the effects of PSC's on other remote sensors.

E. Journal Publications:

None

RESEARCH SUMMARY

TITLE:

A Scientific Planning Meeting on the Study of Gravity Waves and Turbulence in the Middle Atmosphere

INVESTIGATORS AND INSTITUTIONS:

D. C. Fritts, Geophysical Institute, University of Alaska, Fairbanks, Alaska
M. A. Geller, Laboratory for Planetary Atmospheres, NASA Goddard Space Flight Center, Greenbelt, Maryland
B. B. Balsley, Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado
M. L. Chanin, Service d'Aeronomie du C.N.R.S., Verrieres le Buisson, France
I. Hirota, Geophysical Institute, Kyoto University, Kyoto, Japan
J. R. Holton, Department of Atmospheric Sciences, University of Washington, Seattle, Washington
S. Kato, Radio Atmospheric Science Center, Kyoto University, Japan
R. S. Lindzen, Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts
M. R. Schoeberl, Laboratory for Planetary Atmospheres, NASA Goddard Space Flight Center, Greenbelt, Maryland
R. A. Vincent, Physics Department, University of Adelaide, Adelaide, South Australia
R. F. Woodman, Instituto Geofisico del Peru, Sector Educacion, Lima, Peru

ABSTRACT:

The objectives of the workshop were both to review the current theoretical understanding and observational capabilities in the study of gravity waves and turbulence in the middle atmosphere and to suggest theoretical and observational studies that would further our knowledge of these processes and their effects on the large-scale circulation. The review and recommendations were intended to assist in the formulation and design of future studies of middle atmosphere dynamics.

SUMMARY:

Workshop participants reviewed the theoretical, modeling, and observational studies that have contributed to our current knowledge of gravity wave and turbulence processes in the middle atmosphere. Although our detailed knowledge is still very primitive, it is now recognized that the transport and deposition of momentum and energy by gravity waves and turbulent processes is fundamental to the large-scale circulation of the middle atmosphere. Workshop recommendations included additional theoretical and modeling studies of gravity wave excitation, propagation, filtering through wave-wave and wave-mean flow interactions, and the nature and variability of saturation including transient and localization effects. Observational studies were recognized to be important in the determination of the dominant gravity wave sources, wavelength and phase velocity distributions, and momentum and heat fluxes, as well as the temporal and geographical variability of these quantities. Case studies of gravity wave propagation and dissipation as well as measurements of the mean zonal and meridional motions were also thought to be important. Combinations of the various instrumental systems presently available were judged to be of particular utility for the simultaneous measurement of wind and temperature fluctuations due to gravity waves and turbulence.

JOURNAL PUBLICATION:

Fritts, D. C., M. A. Geller, B. B. Balsley, M. L. Chanin, I. Hirota, J. R. Holton, S. Kato, R. S. Lindzen, M. R. Schoeberl, R. A. Vincent and R. F. Woodman, Research Status and Recommendations from the Alaska Workshop on Gravity Waves and Turbulence in the Middle Atmosphere, submitted to AMS Bulletin.

A. TITLE: Mission And Sampling Analyses For Atmospheric Satellite Experiments

B. INVESTIGATORS: G. F. Lawrence
E. F. Harrison

C. ABSTRACT OF RESEARCH OBJECTIVES:

Orbital analyses, instrument-viewing geometry studies, and sampling simulations are performed to define mission concepts for advanced atmospheric research satellite experiments. These analyses are conducted in collaboration with working groups consisting of atmospheric scientists and experiment developers. Analytical techniques are developed and used to optimize sensor-viewing geometries, data gathering strategies, sampling schemes, orbital characteristics, satellite launch times and operational modes of the various experiments and mission concepts. Short-term (7 days) Shuttle Spacelab missions, long-term (1-2 years) satellite missions and multi-satellite (2 and 3 satellites) missions are being studied. Atmospheric experiments which are being analyzed include nadir-viewing sounders, limb emission scanners, laser systems and solar-occultation techniques.

D. SUMMARY OF PROGRESS AND RESULTS

A detailed orbital analysis for the Upper Atmospheric Research Satellite (UARS) was performed and documented in a mission-handbook format (Ref. 1). In this study, specific mission operational constraints and selected UARS sensor characteristics were analyzed. Space and time coverage was generated parametrically and modeled for a set of UARS experiments having different viewing directions (i.e., Nadir, Sun, limb forward and limb side viewing) and different sensor scanning characteristics. Results show that the spatial resolution and key geographical and temporal coverage requirements defined by the UARS science objectives can be satisfied. Latitudinal coverage between 80°N to 80°S is obtained with the solar occulation experiment during the year. The UARS limb-thermal emission instruments can view latitudes up to 80° for a crosstrack scanner. For a limb scanner with a fixed azimuth position (e.g., 90°), the maximum latitude coverage is 80° in one hemisphere and only 32° in the other. Launch time can be selected to ensure good Northern Hemisphere coverage for any designated 40-day period during the critical winter season. In addition, coverage of the winter Northern Hemisphere by limb emission instruments can be significantly improved by modifying the nominal spacecraft azimuthal rotation sequence.

Another mission analysis study was performed which investigated the effects of cloud cover on the number of measurements obtained from a 7-day Shuttle Spacelab-Lidar mission. This analysis combined an empirical global cloud-cover model with an orbital sampling techniques, and study results are presented for the global cloud cover case and one regional (i.e., Continental United States) cloud cover case (Ref.2). Since the science objectives of the Lidar experiment can either emphasize the observation of clouds or clear-sky atmospheric properties, both maximum and minimum cloud-cover conditions were considered in the analysis. Study results show that for the global cloud cover cases, the major influence on the number of measurements obtained is in the selection of the launch month. However, for regional cloud cover cases (i.e., orbital coverage over Continental U.S.) measurements can vary as much as 40 percent depending upon the launch time of day. Launch time of day has a major effect on the number of measurements taken over a region because cloud cover varies diurnally and changes in launch time directly affect the time of satellite passage. Therefore, changes in launch time, in the extreme, can change regional coverage from all daylight measurements to all nighttime measurements for short duration, 7-day Shuttle missions. Cloud cover and number of measurements can be modified to best suit the experiment objectives by proper selection of launch time of day.

E. REFERENCES

1. Lawrence, George F.; Harrison, Edwin F.; and Gibson, Gary G.: "Optimizing Spatial Coverage for UARS Experiments Considering Design and Operational Constraints". (NASA report in progress)

2. Lawrence, George F. and Robbins, John: "The Effects of Cloud Cover on Measurement Opportunities on a Shuttle-Spacelab Lidar Mission." (Report in progress)